15-3324

University of Michigan

JOURNAL

OF

University of Michigan

THE CHEMICAL SOCIETY.

Committee of Publication:

H. E. Armstrong, Ph.D., F.R.S.
W. Crookes, F.R.S.
E. Frankland, D.C.L., F.R.S.
J. H. Gladstone, Ph.D., F.R.S.
C. W. Heaton, F.C.S.
Hugo Müller, Ph.D., F.R.S.
W. H. Perkin, F.R.S.
W. J. Russell, Ph.D., F.R.S.
R. V. Tuson, F.C.S.
R. Warington, F.C.S.
C. R. A. Wright, D.Sc.

Editor:
Henry Watts, B.A., F.R.S.

Sub-Editor:
C. E. Groves, F.C.S.

University of Michigan

Vol. XXXIII.

1878. TRANSACTIONS.

LONDON:
J. VAN VOORST, 1, PATERNOSTER ROW.
1878.

H

LONDON:
HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.

CONTENTS.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

PAGE

I.—First Report to the Chemical Society on Researches on some Points in Chemical Dynamics: by C. R. Alder Wright, DSc., and A. P. Luff 1

II.—Influence exerted by Time and Mass in certain Reactions in which Insoluble Salts are produced: by M. M. Pattison Muir, F.R.S.E. 27

III.—The Chemistry of Cocoa-Butter.—Part I. Two New Fatty Acids: by Charles T. Kingzett 38

IV.—On Nitrification: by Robert Warington 44

V.—The Gas of the "Grotta del Cane," near Naples: by T. Graham Young 51

VI.—On some Derivatives of Allylacetone. By J. K. Crow . 53

VII.—Note on Tetrabromide of Tin. By Thomas Carnelley, D. Sc., and L. T. O'Shea 55

VIII.—On Potable Waters. By Edmund J. Mills, D. Sc., F.R.S. 57

IX.—On a fourth Method for estimating Bismuth volumetrically. By M. M. Pattison Muir, F.R.S.E. 70

X.—On Cuprous Chloride and the Absorption of Carbonic Oxide and Hydrochloric Acid Gas. By J. W. Thomas . . 72

XI.—On Citric Acid as a constituent of the Juice of Unripe Mulberries. By C. R. Alder Wright, D. Sc., and Geo. Patterson 78

XII.—On the Hydrocarbons obtained from the *Pinus sylvestris*, with remarks on the Constitution of the Terpenes. By William A. Tilden, D. Sc. 80

XIII.—On the Luminosity of Benzol when burnt with Non-luminous Combustible Gases. By E. Frankland, F.R.S., and L. Thorne, Jodrell Scholar 89

XIV.—Action of Reducing Agents on Potassium Permanganate. By Francis Jones, F.R.S.E. 95

XV.—On the Decomposition-products of Quinine. By W. Ramsay, Ph.D., Tutorial Assistant of Chemistry, Glasgow University; and J. J. Dobbie, M.A., Clark Scholar in Nat. Sc., Glasgow University 102

XVI.—On the Estimation of Phosphorus in Iron and Steel. By Edward Riley 104

PAGE

XVII.—The Action of Sulphuric Acid on Copper. By Spencer Pickering 112

XVIII.—An Inquiry into the Action of the Copper-zinc Couple on Alkaline Oxy-salts. By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe, F.C.S., Lecturer on Chemistry in Dulwich College 139

XIX.—The Alkaloïds of the Aconites. Part II. On the Alkaloïds contained in *Aconitum Ferox*. By C. R. Alder Wright, D.Sc., Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry in St. Mary's Hospital Medical School 151

XX.—On a Simplification of Regnault's Method for Determining Boiling Points with small quantities of Substance. By H. Chapman Jones, F.C.S. 175

XXI.—On certain Polyiodides. By George Stillingfleet Johnson, Daniell Scholar of King's College, London . 183

XXII.—On Certain Bismuth Compounds. Part VII. By M. M. Pattison Muir, F.R.S.E., Prælector in Chemistry, Caius College, Cambridge 192

XXIII.—On Aromatic Nitrosamines. By Otto N. Witt, Ph.D. 202

XXIV.—On some New Derivatives of Anisoïl (Anisol). By W. H. Perkin, F.R.S. 211

XXV.—Note on the Action of Ammonia on Anthrapurpurin. By W. H. Perkin, F.R.S. 216

XXVI.—Notes on the Tannins. By B. H. Paul, Ph.D., and C. T. Kingzett 217

Anniversary Meeting 221

Balance Sheet 243

XXVII.—A new Process for the Volumetric Estimation of Cyanides. By J. B. Hannay, F.R.S.E. 245

XXVIII.—On Terpin and Terpinol. By William A. Tilden, D.Sc. 247

XXIX.—The Poisonous Principle of *Urechites suberecta*. By J. J. Bowrey 252

XXX.—Note on a new Manganese Reaction. By J. B. Hannay, F.R.S.E. 269

XXXI.—High Melting Points. Part IV. By Thomas Carnelley, D.Sc. 273

XXXII.—On the Determination of High Boiling Points. By T. Carnelley, D.Sc., and W. Carleton-Williams . . 281

XXXIII.—On the Action of Bromine upon Sulphur. By J. B. Hannay, F.R.S.E. 284

XXXIV.—On Essential Oil of Sage. By S. Siguira and M. M. Pattison Muir 292

PAGE

XXXV.—On the Detection and Estimation of Free Mineral Acids in various Commercial Products. By Peter Spence, F.C.S., and A. Esilman 298

XXXVI.—Action of Hypochlorites on Urea. By H. J. H. Fenton, B.A. 300

XXXVII.—On the Behaviour of Metallic Solutions with Filter Paper, and on the Detection of Cadmium. By Thomas Bayley, Assoc. R.C.Sc.I. 304

XXXVIII.—Analogies between the Action of the Copper-Zinc Couple and of Occluded and Nascent Hydrogen. By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe, Lecturer on Chemistry in Dulwich College 306

XXXIX.—The Temperatures at which some of the Alkaloïds, &c., Sublime, as determined by an Improved Method. By A. Wynter Blyth 313

XL.—The Alkaloïds of the Aconites. Part III. By C. R. Alder Wright, D.Sc. (Lond.), Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry in St. Mary's Hospital Medical School 318

XLI.—The Alkaloïds of the Veratrums. Part I. The Alkaloïds of *Veratrum Sabadilla* (Asagrœa officinalis). By C. R. Alder Wright, D.Sc. (Lond.), Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry in St. Mary's Hospital Medical School 338

XLII.—On the Action of Oxides on Salts. Part I. By Edmund J. Mills, D.Sc., F.R.S., "Young" Professor of Technical Chemistry in Anderson's College, Glasgow, and David Wilson 360

XLIII.—Action of Hydrochloric Acid upon Various Metallic Salts. By J. W. Thomas 367

XLIV.—On the Chemical Aspect of Vegetable Physiology. By Sydney H. Vines, B.A., F.L.S., Fellow of Christ's College, Cambridge 375

XLV.—On some Fluorine-compounds of Vanadium. By H. Baker, Student in the Chemical Laboratories of Owens College, Manchester 388

XLVI.—On Ammonium Triiodide. By George Stillingfleet Johnson, Daniell Scholar of King's College, London . . 397

XLVII.—On the Preparation of Salts of Nitrous Oxide. By A. E. Menke, Student in the Laboratory of King's College, London 401

XLVIII.—Action of the Halogens at High Temperatures upon Metallic Oxides. By C. F. Cross and S. Suguira, Students in the Chemical Laboratories of The Owens College . 405

XLIX.—On Manganese Tetrachloride. By W. W. Fisher, M.A., Aldrichian Demonstrator of Chemistry, Oxford . . 409

PAGE

L.—Contributions to the History of the Naphthalene Series. No. II. β-Naphthaquinone. By John Stenhouse, LL.D., F.R.S., and Charles E. Groves 415

LI.—Notes on Madder Colouring Matters. (Continuation.) By Edward Schunck, Ph.D., F.R.S., and Hermann Roemer, Ph.D. 422

LII.—On Pyrotritartaric and Carbopyrotritartaric Acids, Products of the Action of Dilute Sulphuric Acid on Diacetosuccinic Ether. By George H. U. Harrow, Ph.D. . . 425

LIII.—A New Test for Glycerin. By A. Senier, M.D., and A. J. G. Lowe, Assistants in the Laboratories of the Pharmaceutical Society 438

LIV.—On the Preparation of Metallic Chlorides. By Charles W. Watts, of University College, London, and Chichester A. Bell, B.A., M.B. 442

LV.—Laboratory Experiences on board the "Challenger." By J. Y. Buchanan 445

LVI.—The Action of Alkaline Hypobromite on Ammonium Salts, Urea, and Oxamide. Part I. By William Foster, B.A., Lecturer on Chemistry, Middlesex Hospital Medical College. 470

LVII.—On the Part played by Carbon in reducing the Sulphates of the Alkalis. By James Mactear, of St. Rollox Works, Glasgow 475

LVIII.—On the Determination of the Index of Refraction of Liquids by means of the Microscope. By H. C. Sorby, F.R.S., President of the Geological Society 487

LIX.—On the Action of Sodium on the Benzyl Ether of Isobutyric Acid. By W. R. Hodgkinson, Ph.D. 495

LX.—Second Report to the Chemical Society on "Researches on some Points in Chemical Dynamics." By C. R. Alder Wright, D.Sc. (Lond.), Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry, in St. Mary's Hospital Medical School 504

LXI.—Note on the Constitution of the Olefine produced by the Action of Zinc upon Ethylic Iodide. By E. Frankland, D.C.L., F.R.S., and Leonard Dobbin, Esq. 545

Proceedings at the Meetings of the Chemical Society, Session 1877–78 547

Donations to the Library, 1877–78 552

JOURNAL

OF

THE CHEMICAL SOCIETY.

University of Michigan

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*First Report to the Chemical Society on "Researches on some Points in Chemical Dynamics."*

By C. R. Alder Wright, DSc. (Lond.), Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry, in St. Mary's Hospital Medical School.

§ 1. Introductory.

From certain theoretical speculations, it appeared probable to us that in cases of actions of single decomposition typified by the equation—

$$A + BC = AB + C,$$

the temperature at which the action commences is a function (I) of the physical condition of the bodies experimented with; (II) of the heat-disturbance (*i.e.*, evolution or absorption—wärmetönung) occurring during the reaction; and (III) of other chemical habitudes of the substances concerned, possibly expressible as numerical values constant for each substance.

(I.) That the temperature of initial action of a given body A, on a given compound BC, varies to an appreciable though not an enormous extent with the physical condition of the compound BC, is not only highly probable, *à priori*, but has been demonstrated to be the case in the instance of carbon oxide acting on ferric oxide, by I. Lowthian Bell,* with whom one of us co-operated in the inquiry. According as the ferric oxide had been prepared by a wet process, or by ignition of ferrous sulphate, and according as it was pure or intermixed with

* "Chemical Phenomena of Iron Smelting," by I. Lowthian Bell, F.R.S., M.P. Routledge and Sons. Page 13, *et seq.*

inert earthy matters (as in the case of various iron ores), it was found that the temperature at which pure carbon oxide first began to take away oxygen from the ferric oxide forming carbon dioxide varied between 141° and 211°. It is a matter of everyday experience that hard compact substances are little if at all affected by various chemical agents, under circumstances where action is readily brought about if these substances be in different physical states as to aggregation of particles, &c., although determinations of the temperatures at which action commences in these different instances have for the most part not yet been made.

(II.) As regards this speculation, little if any trustworthy information of an experimental kind is extant. Lowthian Bell has shown (*loc. cit.*, p. 91) that carbon oxide does not act on zinc oxide at 420°, whilst it reduces lead oxide completely at that temperature. Now the heat disturbance during the reaction—

$$ZnO + CO = Zn + CO_2,$$

must have a lower value than that during the reaction—

$$PbO + CO = Pb + CO_2,$$

because the "heat of combustion" of zinc is greater than that of lead, whence less heat must be evolved in the reduction of zinc oxide by a given reducing agent than in that of lead oxide. In order to see if it is a general rule that, *cæteris paribus*, the temperature at which a reducing action commences is lower the greater the algebraic value of the heat disturbance taking place during its occurrence (*i.e.*, the less the heat absorption, or the greater the heat evolution taking place), the experiments detailed in this report were made.

(III.) That the temperature at which action commences is influenced by other chemical habitudes of the bodies involved besides their "heats of combustion" (and their physical state), is rendered probable by the observation of Lowthian Bell (*loc. cit.*, pp. 13 and 91), that stannic oxide is unaffected by carbon oxide at 420°, whilst ferric oxide is acted on at much lower temperature (141° to 211°, according to the physical state); for the "heat of combustion" of tin is nearly the same as that of iron (reckoned per equal quantities of oxygen consumed): viz., according to Andrews:—

	Tin.	Iron.
Heat evolved in uniting with 1 gram of oxygen ..	4230	4153

from which it might be expected that the action of carbon oxide on tin oxide and on iron oxide would commence at temperatures not far apart. It would result from this that if numerical values, "constants of chemical activity," be really assignable to each substance, the constant for stannic oxide must differ considerably from that for ferric oxide.

In order to trace out the relationships (if any) which exist between the heat disturbances during reactions of the form—

$$A + BC = AB + C,$$

and the temperatures at which these actions are first noticeable, a series of observations have been made as to the temperatures at which the reducing actions commence of the three agents, carbon oxide, hydrogen, and finely divided carbon, on the oxides of copper and iron in different physical conditions, with the result of substantiating the general correctness of the rule, that *the lower the algebraic value of the heat disturbance, the higher the temperature of initial action*, so far as these bodies are concerned. Thus during the reactions—

$$\begin{aligned} &(1) \ldots\ldots \quad CuO + CO = Cu + CO_2 \\ &(2) \ldots\ldots \quad CuO + H_2 = Cu + H_2O \\ &(3) \ldots\ldots \quad 2CuO + C = 2Cu + CO_2, \end{aligned}$$

the heat disturbances are (per 16 grams of oxygen transferred) + 30·05, + 19·52, and + 9·48 kilogram heat-units respectively; with a given specimen of copper oxide (*i.e.*, with a constant physical state), the reducing action of carbon oxide is uniformly manifested at a lower temperature than that of hydrogen, and that of hydrogen is noticeable at a lower temperature than that of carbon. With cuprous and ferric oxides, and these three reducing agents, the same order of sequence is observed; whilst on comparing the temperatures of initial action of these reagents on oxide of copper and oxide of iron in analogous physical states, it is found that each reducing agent begins to act on copper oxide at a lower temperature than on iron oxide, the heat disturbances during the reduction of ferric oxide by these three agents being respectively + 1·90, −8·63, and −18·67, or considerably less in each instance than with copper oxide and the same reducing agent respectively.

§ 2. Calculation of Heat Disturbances during Reduction of Oxides of Copper and Iron by Carbon Oxide, Hydrogen, and Carbon.

The numerical values just cited as the calculated heat disturbances are deduced from the following data; they represent the heat evolutions or absorptions that would ensue if the metallic oxides were reduced in such a way that all the materials and products were examined at the same temperature, viz., about 15° C.; as shown further on, little difference in the relative values is caused by recalculating the numbers, on the supposition that the action takes place at some more elevated temperature, say 200° or 300°.

Let H_1 be the heat evolved by copper in uniting with 16 grams of oxygen to form cupric oxide.

H_2 that evolved by CO in uniting with 16 grams of oxygen to form CO_2.

H_3 that evolved by hydrogen in uniting with 16 grams of oxygen to form H_2O.

And H_4 that evolved by carbon in uniting with 16 grams of oxygen to form CO_2.

Then the heat disturbances taking place during the reactions—

$$\begin{aligned} &(1) \ldots\ldots \quad CuO + CO = Cu + CO_2 \\ &(2) \ldots\ldots \quad CuO + H_2 = Cu + H_2O \\ &(3) \ldots\ldots \quad 2CuO + C = 2Cu + CO_2, \end{aligned}$$

are respectively:—(1) H_2-H_1; (2) H_3-H_1; and (3) H_4-H_1.

Now H_1 was found by Andrews to be 38·30 kilogram heat-units. For H_2 the following values have been found:—

$$\begin{aligned} &28 \times 2{\cdot}431 \text{ (Andrews.)} \\ &28 \times 2{\cdot}403 \text{ (Favre and Silbermann.)} \\ &28 \times 2{\cdot}490 \text{ (Dulong.)} \\ \text{Mean } &28 \times 2{\cdot}441 = 68{\cdot}35. \end{aligned}$$

Again, for H_3 the value $2 \times 34{\cdot}275 = 68{\cdot}55$ is found as the mean value deduced from the experiments of Hess, Dulong, Grassi, Favre, and Silbermann, Julius Thomsen, Andrews, and Joule.* This number expresses the "heat of combustion of hydrogen," assuming that *water* is formed; if, however, *aqueous vapour* be produced, as is the case in the experiments that follow, this value is too high by $18 \times 0{\cdot}596 = 10{\cdot}73$, where 0·596 is the latent heat (in kilogram heat-units) of aqueous vapour at 15° (Regnault). Hence

$$H_3 = 68{\cdot}55 - 10{\cdot}73 = 57{\cdot}82.$$

Similarly for H_4 the following values have been found (for amorphous carbon):—

$$\begin{aligned} &6 \times 8{\cdot}080 \text{ (Favre and Silbermann.)} \\ &6 \times 7{\cdot}912 \text{ (Despretz.)} \\ &6 \times 7{\cdot}900 \text{ (Andrews.)} \\ \text{Mean } &6 \times 7{\cdot}964 = 47{\cdot}78 \end{aligned}$$

* *Vide* Alder Wright, *Phil. Mag.*, Dec., 1874. This number is practically the same as those found recently by von Than, and by Schuller and v. Wartha (*Deut. Chem. Ges. Ber.*, 1877, 947 and 1298); the first of whom obtained the values $2 \times 33{\cdot}982$ and $2 \times 34{\cdot}041$, whilst the latter observers found $2 \times 34{\cdot}126$, when 2 grams of hydrogen and 15·96 grams of oxygen (Stas) at 0° are burnt to water at 0°.

Hence the heat disturbances during the above three reactions are—

$$(1)\ H_2 - H_1 = 68{\cdot}35 - 38{\cdot}30 = + 30{\cdot}05$$
$$(2)\ H_3 - H_1 = 57{\cdot}82 - 38{\cdot}30 = + 19{\cdot}52$$
$$(3)\ H_4 - H_1 = 47{\cdot}78 - 38{\cdot}30 = + 9{\cdot}48$$

In just the same way the heat disturbances during the reduction of iron oxide are calculated; the "heat of combustion" of iron, per 16 grams of oxygen added on, was found by Andrews to be $16 \times 4{\cdot}153 = 66{\cdot}45$ kilogram heat-units; whence the heat disturbances during reduction by carbon oxide, hydrogen, and carbon are respectively—

$$68{\cdot}35 - 66{\cdot}45 = + 1{\cdot}90$$
$$57{\cdot}82 - 66{\cdot}45 = - 8{\cdot}63$$
$$47{\cdot}78 - 66{\cdot}45 = - 18{\cdot}67$$

In order to recalculate from these numbers the heat disturbances taking place at any other temperature, say T°, the following formula must be employed:—

$$H_T = H_{15} + h_1 + h_2 - (h_3 + h_4),$$

where H_T is the recalculated heat disturbance at T°.

H_{15} is that found as above at 15°.

h_1 is the heat required to raise the temperature of the metallic oxide from 15° to T.

h_2 is the heat required to raise the temperature of the reducing agent from 15° to T.

h_3 is the heat required to raise the temperature of the reduced metal from 15° to T.

And h_4 is the heat required to raise the temperature of the complementary product from 15° to T.

h_1, h_2, h_3, and h_4 are obtained by means of the formula—

$$h = W \times S \times (T - 15)$$

Where W is the weight of substance heated (in kilos.), and S its mean specific heat between 15° and T°. Since W and S are tolerably small fractions, the value of h_1, h_2, h_3, h_4 are necessarily not very large, so that the differential correction, $h_1 + h_2 - (h_3 + h_4)$ is but small. Thus if T be taken as 215° (so that $T - 15 = 200°$, this number being taken to simplify calculation) the values of H_T for the three cases of reduction of copper oxide by carbon oxide, hydrogen, and carbon become respectively—

For Carbon Oxide—

Value of W. Value of S.

$$H_{215} = H_{15} + \left.\begin{array}{l} 0{\cdot}0795 \times 0{\cdot}142 \times 200 \\ + 0{\cdot}028 \times 0{\cdot}245 \times 200 \\ - 0{\cdot}0635 \times 0{\cdot}095 \times 200 \\ - 0{\cdot}044 \times 0{\cdot}216 \times 200 \end{array}\right\} = \left\{\begin{array}{r} H_{15} + 2{\cdot}26 \\ + 1{\cdot}37 \\ - 1{\cdot}21 \\ - 1{\cdot}90 \end{array}\right\} = H_{15} + 0{\cdot}52$$

For Hydrogen—

$$H_{215} = H_{15} + \left.\begin{array}{l} 0{\cdot}0795 \times 0{\cdot}142 \times 200 \\ + 0{\cdot}002 \times 3{\cdot}409 \times 200 \\ - 0{\cdot}0635 \times 0{\cdot}095 \times 200 \\ - 0{\cdot}018 \times 0{\cdot}4805 \times 200 \end{array}\right\} = \left\{\begin{array}{r} H_{15} + 2{\cdot}26 \\ + 1{\cdot}36 \\ - 1{\cdot}21 \\ - 1{\cdot}73 \end{array}\right\} = H_{15} + 0{\cdot}68$$

For Carbon—

$$H_{215} = H_{15} + \left.\begin{array}{l} 0{\cdot}0795 \times 0{\cdot}142 \times 200 \\ + 0{\cdot}006 \times 0{\cdot}2415 \times 200 \\ - 0{\cdot}0635 \times 0{\cdot}095 \times 200 \\ - 0{\cdot}022 \times 0{\cdot}216 \times 200 \end{array}\right\} = \left\{\begin{array}{r} H_{15} + 2{\cdot}26 \\ + 0{\cdot}29 \\ - 0{\cdot}21 \\ - 0{\cdot}95 \end{array}\right\} = H_{15} + 0{\cdot}39$$

It is manifest that the three values $H_{15} + 0{\cdot}52$, $H_{15} + 0{\cdot}68$, and $H_{15} + 0{\cdot}39$ (or 30·57, 20·20, and 9·87) are in the same order of magnitude as the values of H_{15} itself, viz., 30·05, 19·52, and 9·48. The *average* increment of the three cases, $\frac{0{\cdot}52 + 0{\cdot}68 + 0{\cdot}39}{3} = 0{\cdot}53$, is so near to each one increment severally, that the difference is much less than may readily be attributed to inexact values being taken for S, the values assumed above not representing exactly the *mean specific heats between* 15° *and* 215°, but only approximations thereto, being mainly the mean specific heats found for somewhat different ranges of temperature.

§ 3. Preparation of Metallic Oxides in Different Physical States.

(I.) *Cupric Oxide.*

Three varieties of cupric oxide in as pure a form as possible were employed throughout the whole series of experiments; these were obtained as follows:—

Specimen A.—Electrolytic copper was dissolved in nitric acid and precipitated by a solution of caustic potash, well boiled, filtered, and *thoroughly* washed and dried at 130°. In order to prevent the taking up of organic matter by the copper oxide, it was found absolutely indispensable to employ washing water freed from organic matter by careful re-distillation, and potash that had been fused at a red heat before use; glass-wool, or asbestos filters only were employed. In several preliminary experiments much time was lost through the use

of oxides of copper and iron containing traces of organic matters derived from one source or other; these oxides were found to evolve small quantities of carbon dioxide on heating to redness *in vacuo*, which necessarily vitiated the determinations of the temperature at which carbon begins to reduce these metallic oxides (§ 6).

Specimen B.—Copper nitrate (from electrolytic copper), carefully ignited till completely converted into oxide and retaining no oxide of nitrogen.

Specimen C.—Electrolytic copper, in thin slips, roasted for many days at a bright red heat in a porcelain tube, through which air was aspirated. The lumps of oxide thus produced were crushed, metallic particles picked out, and the whole again roasted in a current of air, and finally in oxygen, at a bright red heat, for several hours. Even after several repetitions of the roasting, it was not found practicable to obtain a material containing exactly the amount of oxygen to form cupric oxide; the substance ultimately obtained was finely powdered, thoroughly intermixed, and analysed with the result of finding that the oxygen present was exactly 98·5 per cent. of that required to form CuO, *i.e.*, that the composition was $Cu_{200}O_{197}$, or $194CuO,3Cu_2O$: the deficiency in oxygen was determined by dissolving known weights in a mixture of hydrochloric acid and ferric chloride, diluting with boiled water, and titrating by permanganate. As stated below (§ 5), this method was found to give very constant results, and was employed, in many cases, to decide whether deoxidation of copper oxide had commenced, and to what amount it had gone on.

Besides these, several other specimens of copper oxide were used for comparison in some of the experiments (*vide* § 4).

(II.) *Cuprous Oxide.*

According to Andrews, the "heat of combustion" (per constant quantity of oxygen) of copper to cuprous oxide is almost identical with that to cupric oxide, viz., per 16 grams of oxygen :—

Copper to cupric oxide	38·30	kilogram heat-units
„ cuprous „	36·61	„ „

It should therefore result, if the hypothesis be correct that the temperature of initial action is (*cæteris paribus*) lower the greater the heat evolution (algebraically), that cuprous and cupric oxides should be acted on by each reducing agent at about the same temperature, their physical states being identical. As shown below, this appears to be the case.

Cuprous oxide was prepared perfectly free from organic matter by dissolving cane-sugar in water, filtering, and inverting by boiling

with sulphuric acid; electrolytic copper converted into nitrate was boiled with potash (recently fused at a red heat) and this inverted sugar, and the red cuprous oxide precipitated, thoroughly washed with water free from organic matter. Several other samples of cuprous oxide were prepared in other ways, such as reduction by a filtered solution of commercial glucose, &c.; but these invariably retained more or less organic matter, and evolved CO_2 on heating to redness *in vacuo;* some absorbed oxygen whilst drying, and much labour was expended before a good sample was obtained. On analysis, the pure cuprous oxide was found to contain 99·7 per cent. of Cu_2O, the process adopted being titration with permanganate as above described; it gave off no trace of CO_2 on heating to redness in a Sprengel vacuum.

(III.) *Ferric Oxide.*

Three varieties of ferric oxide were used in the experiments with this substance.

Specimen A.—Pure ferrous sulphate was recrystallised several times, dehydrated, and strongly calcined for some hours till wholly converted into ferric oxide; the compact granular substance produced was ground in a mortar to a fine powder.

Specimen B.—Ferric oxide prepared by calcining the sulphate was dissolved in boiling hydrochloric acid, and the solution poured into excess of ammonia water: the precipitate was boiled and thoroughly washed till no trace of chlorine was present in the wash waters; after drying in the water-bath, it was rendered anhydrous, or almost absolutely so, by long-continued heating at 180—200°.

Specimen C.—Ferric oxide B was strongly ignited in a platinum crucible for a few minutes; it shrank considerably in bulk, and became darker and less readily soluble in hydrochloric acid.

Several other specimens were previously prepared by precipitation of ferric salts, such as the filtered solutions of commercial chloride, &c.; but these were found to contain traces of organic matter derived either from the materials or the wash water, as they gave off more or less carbon dioxide on heating to redness in a Sprengel vacuum. The above three specimens, however, were found to be free from organic matter by this test; and after heating in a test-tube to 300—400°, they were not in any way reduced, no blue colour being given on solution in hydrochloric acid and addition of ferricyanide.

§ 4. Determination of Temperature of Initial Action of Carbon Oxide on Copper and Iron Oxides.

The metallic oxides were placed in a test-tube arranged vertically in a paraffin bath, about 0·5 gram being taken for each observation:

the mouth of the test-tube was closed by a cork with three perforations; one for a thermometer, the bulb of which reached down to the bottom; one for an entrance-tube for leading in pure carbon oxide, also reaching to the bottom; and the third for an exit-tube just passing though the cork, and bent externally to a right angle and coupled by an india-rubber joint to a Will and Varrentrapp's ammonia-bulb apparatus filled with clear baryta-water. In order to make sure that the entering carbon oxide had the same temperature as the bath, the entrance-tube was bent over downwards and upwards so as to form a **U** reaching down to about the bottom of the test-tube, and lying close to the outer surface; the upper bend of this tube between the cork and the **U** was wrapped with lamp-wick to avoid aërial cooling. By keeping the baths at various fixed temperatures and passing carbon oxide through for a few minutes, the temperature of initial action was approximately found by noticing at what temperature the baryta-water first became turbid; and then by repeating the observations several times with fresh portions of metallic oxide, still nearer temperature-readings were obtained: the differences observed between several careful determinations rarely exceeded a degree above or below the mean.

The carbon oxide employed was generated from ferrocyanide and sulphuric acid being washed through caustic soda, silver nitrate, and sulphuric acid, and stored in a gasholder over water: the gas thus kept in stock invariably contained a little air, probably derived from that absorbed by the water. As some of the experiments showed (§ 4 *infra*) that a partially reduced metallic oxide sometimes causes a kind of catalytic oxidation of carbon oxide to dioxide when a mixture of carbon oxide and a little air is led over it, it is possible that the original unreduced metallic oxide might to some extent possess the same power; wherefore, before use, the free oxygen in the carbon oxide was removed by passing the gas from the gasholder through a tube filled with fragments of well-burnt charcoal, and heated red-hot by a small gas-furnace, and then through a series of Liebig's bulbs containing caustic potash and potassium pyrogallate. In this way carbon oxide, absolutely free from all trace of admixed oxygen, was obtained, but containing a small percentage of free nitrogen. It is noteworthy that a red-hot tube filled with pumice-stone did *not* cause the removal of all free oxygen (by conversion into carbon dioxide) from the air containing carbon oxide, whilst the same tube filled with charcoal fragments completely removed all free oxygen unless the stream of gas were considerably rapid. The issuing gas, however, contained carbon dioxide in notable quantity, the reducing action of the charcoal on the carbon dioxide not being sufficiently great to re-convert all of that gas into carbon oxide; hence, potash-bulbs to

purify the issuing gas from carbon dioxide were indispensable, although the pyrogallate tubes were only requisite as an additional precaution.

In this way, the following numbers were obtained as the mean results from several trials in each instance:—

Cupric Oxide.

	Specimen A.	Specimen B.	Specimen C.
Temperature at which turbidity was first produced in baryta-water after from three to five minutes.....	60°	125°	146°
Temperature at which action was well marked (considerable turbidity produced by a few bubbles of issuing gas).....	68°	133°	150°

Very similar numbers were obtained with other samples of cupric oxide prepared in similar ways, but not so pure; although some of these contained traces of organic matter, yet none of them evolved any carbon dioxide on heating in a current of air to a temperature higher than that at which carbon dioxide was freely formed on heating in carbon oxide. Thus, three other specimens gave these numbers: D, prepared by precipitation from recrystallised commercial copper sulphate, washing, and drying at 130°; E, by ignition of commercial copper nitrate; and F, roasted copper wire, as sold for combustion analyses, powdered in a mortar.

	Specimen D.	Specimen E.	Specimen F.
Temperature of first turbidity	68°	125°	137°
Temperature of well marked action	85°	133°	142°

Cuprous Oxide.

Besides the pure cuprous oxide described above, two other specimens were also examined so far as the temperature of initial action of carbon oxide is concerned; one prepared by precipitation of copper nitrate by glucose and potash, and one purchased from Messrs. Hopkin and Williams: each of these two contained small quantities of organic matter, but gave off no carbon dioxide on heating in a current of air to temperatures above those where the reducing action of carbon oxide is well marked.

	Pure cuprous oxide.	Impure cuprous oxide.	
		By glucose.	From Hopkin and Williams.
Temperature of first turbidity	110°	128°	140°
Temperature of well marked action	120°	136°	150°

Ferric Oxide.

	Specimen A.	Specimen B.	Specimen C.
Temperature of first turbidity	202°	90°	220°
Temperature of well marked action	210°	100°	230°

Two other specimens of ferric oxide, prepared by precipitation, but retaining traces of organic matter, were first acted on at 85° and at 97°, the action being well marked at 100° and 105° respectively.

The above numbers show how considerable an influence on the temperature of initial action is exerted by difference in physical state; this is especially well instanced by specimens B and C of ferric oxide, where simple ignition of B for a few minutes raises the temperature of initial action by 130°. In one experiment some of the copper oxide B had been heated in a porcelain crucible over a Bunsen burner, and the surface had become reduced by the diffusion into the crucible of gases from the flame; on allowing to cool with the lid off, the partially reduced oxide again became black and apparently reoxidised; after cooling, however, the portion constituting the upper film was found to be first acted on by carbon oxide at 97°, the action being well marked at 100°; so that a lowering of some 28° in temperature of initial action was brought about by the alteration in physical structure due to partial reduction and reoxidation at a temperature not very elevated.

The numbers found by Lowthian Bell (*loc. cit.*) as the temperature of initial action of carbon oxide on ferric oxide, prepared by calcining the sulphate, and by precipitation and *gentle* ignition, were respectively 208° and 141°; the above results agree well with the first of these numbers, whilst the numbers found for precipitated oxide dried at 180°, and the same strongly ignited, lie on opposite sides of the value found by Bell in the latter instance.

It deserves notice that the action of carbon oxide on oxide of copper prepared by precipitation, well marked at temperatures considerably below 100°, becomes extremely energetic at 100°: tubes of 50 to 100 c.c. capacity, containing about a gram of the copper oxide and filled with carbon oxide, were sealed and heated to 100° for a few hours; at the end of the time the carbon oxide was wholly converted into carbon dioxide; in one case this result was observed after four hours' heating, in another after two hours at 100°. In order to gain some idea as to the rapidity with which the action goes on at 100°, a slow stream of purified carbon oxide was led over 0·5 gram of cupric oxide (specimen A) in a tube heated in boiling water, and the carbon dioxide produced collected and weighed; in this way the following numbers were obtained:—

Time.	Oxygen removed, that originally present being 100°.
15 minutes	22·6
60 „	49·3
90 „	71·8
120 „	79·8

The loss of oxygen deduced from the loss of weight of the cupric oxide at the end of the time was 82·4, the slight difference being due in all probability to the carrying away of a milligram or two of moisture from the potash bulbs for absorption of CO_2 by the issuing excess of CO. The reduced copper oxide was black and distinctly pyrophoric whilst warm.

In the course of some other experiments of the same kind, it was noticed that when the carbon oxide was not purified from small quantities of admixed air by the method above described, the amount of carbon dioxide collected greatly *exceeded* that corresponding to the loss of weight; thus in two experiments the following numbers were obtained:—

	Time of exposure.	Oxygen removed, calculated from CO_2 found, that originally present being 100°.	Oxygen removed, calculated from loss of weight.
(1)	90 minutes	155·0	71·9
(2)	220 „	113·0	72·0

whence it is evident that either the partially reduced oxide acted catalytically in causing combination between the free oxygen and the carbon oxide in the gaseous mixture, or the nearly reduced oxide took up the free oxygen, and was then again reduced in virtue of the reactions—

$$Cu_xO_y + O = Cu_xO_{y+1}$$
$$Cu_xO_{y+1} + CO = Cu_xO_y + CO_2,$$

thus forming more carbon dioxide than that corresponding to the difference between the original oxygen in the cupric oxide employed, and that left associated with the copper after the action was completed.

§ 5. Determination of Temperature of Initial Action of Hydrogen on Copper and Iron Oxides.

The same arrangement was adopted as that employed as above described in the case of carbon oxide, the baryta-water bulb being omitted; in the case of some few of the observations where the temperature was above about 260° (so that there might be some danger of the cork being charred and vapours given off which might perhaps

reduce the metallic oxide), a simpler arrangement was employed consisting of a narrow glass tube passing horizontally through a hot-air bath, the metallic oxide being placed in the central part of the tube, and the bulb of a thermometer just level with it: to avoid currents of air in the bath, the tube and thermometer-bulb were enclosed in a small inner chamber with perforations just big enough to allow the ends of the tube and the thermometer-bulb to pass through.

The hydrogen was prepared from zinc and sulphuric acid, being passed successively through U-tubes containing pumice-stone soaked in silver nitrate, caustic potash, and sulphuric acid. In order to determine as nearly as possible the temperature of initial action, quantities of about 0·3 gram of metallic oxide were used for each observation; the air-bath having been heated to some given temperature, the hydrogen was turned on and allowed to pass through for 15 minutes; the tube containing the oxide was then removed from the bath and allowed to cool, a current of hydrogen still passing through. The cooled contents were then boiled with hydrochloric acid (in the case of the copper oxides with hydrochloric acid and ferric chloride), the solution diluted with boiled water and tested by ferricyanide or by permanganate; generally weighed quantities of metallic oxide and a standard permanganate solution were employed. Careful tests showed that neither the cupric oxide prepared by precipitation (A), nor that by ignition of the nitrate (B), nor any one of the three kinds of ferric oxide, caused the faintest trace of blue with ferricyanide when tested in this way before exposure to hydrogen or after heating *per se*. As to the copper oxide from roasting of metal (C) and the cuprous oxide, weighed quantities were taken for each trial, and the amount of permanganate corresponding subtracted from that ultimately consumed; it was found that absolutely concordant numbers were obtained in several consecutive blank experiments made to determine the amount of permanganate solution required for the copper oxides before exposure to hydrogen.

In this way the following numbers were obtained, 15 minutes' exposure to hydrogen at the temperature indicated being allowed in each case:—

Copper Oxide (A).

Temperature.	Percentage of oxygen removed (that in original oxide being 100°).
All temperatures up to 83°	No trace.
At ..... 87—90°	1·7
„ ..... 100°	7·0
„ ..... 150°	Almost complete reduction; much red spongy metal formed not readily dissolved by hydrochloric acid and ferric chloride.

Cupric Oxide (B).

Temperature.	Percentage of oxygen removed.
All temperatures up to 170°	No trace.
At ..... 178—180°	4·3
„ ..... 200°	8·8

Cupric Oxide (C).

All temperatures up to 170°	Nil.
At ..... 175°	16·7
„ ..... 220°	Much metal reduced, undissolved by a few minutes' boiling with hydrochloric acid and ferric chloride.

Cuprous Oxide.

All temperatures up to 150°	No trace.
At ..... 160°	27·5
„ ..... 180°	Much metal left undissolved by hydrochloric acid and ferric chloride.

Ferric Oxide (A).

All temperatures up to 255°	No trace.
At ..... 265—270°	1·8
„ ..... 290°	5·6
„ ..... 310°	8·0
„ 360° (in mercury vapour).	16·5

Ferric Oxide (B).

All temperatures up to 190°	No trace.
At ..... 200°	0·7
„ ..... 210°	1·4
„ ..... 250°	7·7

Ferric Oxide (C).

All temperatures up to 240°	No trace.
At ..... 250°	1·2
„ 360° (in mercury vapour).	14·5

From these observations the following temperatures may be taken as close approximations to the temperatures of initial action of hydrogen on these metallic oxides :—

Oxides of Copper.

Cupric oxide (A).	Cupric oxide (B).	Cupric oxide (C).	Cuprous oxide.
85°	175°	172°	155°

Ferric Oxides.

Specimen (A).	Specimen (B).	Specimen (C).
260°	195°	245°

It is noticeable that by plotting out some of the above results, taking the temperatures as ordinates and the percentages of oxygen removed as abscissæ, approximations are obtained to curves which indicate the relative degrees of energy of reducing action of hydrogen at different temperatures. It is proposed to multiply and extend observations of this nature, carefully conducted under precisely the same conditions, save as regards temperature, so as to obtain the data for accurately-determined curves of this kind, not only with hydrogen and copper and iron oxides, but also with other substances.

Three experiments were made by Lowthian Bell (*loc. cit.*, p. 118) by exposing calcined Cleveland ironstone to the action of hydrogen at 104—127° for 30 minutes, at 199—227° for 30 minutes, and at a bright red-heat for four hours respectively. In the first case no reduction whatever was perceptible; in the second a trace of reduction had apparently taken place; whilst in the third much of the ferric oxide was reduced, though not all. The evidence of the trace of reduction in the second case was that the material, after exposure, slightly reduced permanganate when dissolved in acid: it is manifestly possible that this action was due to the presence, in the substance treated, of a minute grain of imperfectly peroxidised ferrous carbonate; still, admitting that the reducing action of hydrogen in this form of impure ferric oxide is just perceptible between 199° and 227°, this result is fairly in accordance with the above observations.

Stromeyer found (*Pogg. Annalen*, vi, 471 [1826]) that ferric oxide (how prepared is not stated) is readily completely deoxidised by hydrogen at a red-heat, reduction commencing at considerably lower temperatures, but not proceeding very rapidly. Magnus found (*ibid.*, vi, 509) that whilst ferric oxide is not appreciably acted on by pure dry hydrogen at the temperature of boiling water, and whilst no visible production of water ensues even on heating in boiling rape oil, *complete* deoxidation ensues in two hours at a temperature close to that of boiling mercury, and at any rate below the temperature of melting zinc.

§ 6. Determination of Temperature of Initial Action of Carbon on Copper and Iron Oxides.

The first preliminary experiments in this direction were made by heating intimate mixtures of the carbon and metallic oxides (ground together in an agate mortar) to various temperatures, and then endeavouring to measure the reduction by solution in hydrochloric acid (or hydrochloric acid and ferric chloride) and titration by permanganate; but so many difficulties occurred in the way of obtaining anything like trustworthy results, that this plan had to be abandoned. In the first place, all kinds of carbon tried produced more or less reduction of ferric chloride when boiled therewith without any metallic oxide at all; and the amount of reduction produced was different after heating to, say, 300° from what it was originally, and was not constant after the heating, so that it was not possible to apply a correction by using weighed quantities of carbon; this was ultimately traced to the power which carbon possesses of occluding gases, and in particular carbon oxide, which in this occluded form seems to act readily as a reducing agent, much as hydrogen, occluded by palladium, possesses high reducing powers. For this same reason, indications of reduction by carbon were obtained at temperatures far lower than those subsequently determined by more accurate methods, the heat causing a certain amount of the occluded carbon oxide to be evolved, and so to act on the metallic oxide. (It is not unlikely, moreover, that occluded air on heating would act on the carbon, thus producing additional carbon oxide.) Direct experiments proved, as described below, that the gases occluded by carbon are not entirely given off in a Sprengel vacuum at the ordinary temperature, notable quantities of carbon oxide and dioxide being extracted by this means on heating after complete exhaustion at the ordinary temperature.

The mode of operation finally adopted was the following:—Batches of carbon were prepared in quantity sufficient to last for a whole series of experiments: the amounts of gas given off by weighed quantities of each kind on heating through certain ranges of temperature after previous complete exhaustion in a Sprengel vacuum at the ordinary temperature were determined once for all (on samples drawn from the bulk after thorough intermixture). Weighed quantities of carbon and metallic oxide were then thoroughly incorporated by continued grinding together in an agate mortar; the mixture was transferred to a suitable tube connected with a Sprengel pump, and the whole exhausted till no more gas was extracted by 5 or 10 minutes' action of the pump. The tube was then heated to a given temperature and maintained thereat for 15 to 30 minutes, and the gas evolved pumped

out, measured, and analysed (when necessary). As long as the bulk of gas thus extracted did not amount to appreciably more than that furnished by the same weight of carbon alone under the same conditions, it was inferred that there was no action between the carbon and the metallic oxide, and the temperature of initial action was taken to be *that temperature at which more gas began to be furnished than that due to the carbon alone, the evolution of gas going on continuously for some time.*

In thus manipulating it was found absolutely necessary to confine the mixture of carbon and metallic oxide in the closed end of the tube by a plug of recently ignited asbestos firmly rammed down, otherwise the evolution of gas from the carbon on exhausting caused a dancing about of particles of carbon in the tube, thus effecting a partial mechanical separation of carbon from metallic oxide; and what was of still more serious moment, caused particles of carbon to be drawn over into the tubes of the Sprengel pump, thus utterly vitiating all measurements by reabsorbing, to a greater or lesser extent, the gas evolved. It was found that after strong ignition the asbestos used for the plug retained so little occluded air, &c., that when the tube was rendered vacuous while cold it practically remained so on heating if nothing but asbestos were present. Many of the earlier observations were spoiled, however, by our omitting this precaution and using asbestos which parted with sensible quantities of gases on heating after rendering the tube vacuous when cold.

Several kinds of carbon were experimented with at first, but many of these were rejected because they contained considerable percentages of hydrogen (even after strong ignition), or on account of inorganic impurities. Two varieties were ultimately selected, which, although not absolutely pure amorphous carbon, were, we believe, as pure as that substance can be practically obtained. One of these was a hard dense coke-like charcoal, prepared by heating recrystallised sugar in closed crucibles, powdering the light charcoal thus obtained, and strongly igniting it in small portions at a time in well-closed platinum crucibles, then igniting it in a current of chlorine for two hours, and finally again igniting it in closed platinum crucibles over a blowpipe for six hours until no trace of hydrochloric acid escaped. The other was an extremely light porous carbon, obtained by passing carbon oxide over ferric oxide at about 400—450° for many hours, whereby (as Lowthian Bell has shown, *loc. cit.*, p. 44) reduction of the carbon oxide to carbon is brought about, to a large extent, by the agency of the lower oxides of iron first formed, thus:—

$$Fe_xO_y + CO = C + Fe_xO_{y+1},$$

the higher oxide thus formed being again reduced by another portion of carbon oxide.

$$Fe_xO_{y+1} + CO = CO_2 + Fe_xO_y.$$

The black mass thus obtained was boiled with dilute hydrochloric acid, thoroughly washed, again boiled with concentrated hydrochloric acid, washed on the pump-filter till the washings were neutral, and finally dried at 100°, and gently ignited in a closed crucible to expel moisture.

On analysis these two samples gave the following numbers:—

From sugar; 0·2575 gram gave 0·9080 CO_2 and 0·0195 H_2O, and left 0·0040 ash; 0·2375 gram gave 0·8285 CO_2 and 0·0160 H_2O, and left 0·0040 ash.

From carbon oxide; 0·2250 gram gave 0·7960 CO_2 and 0·0145 H_2O, and left 0·0020 ash.

	From sugar.		From carbon oxide.
Carbon	96·17	95·13	96·49
Hydrogen.....	0·84	0·75	0·72
Ash	1·56	1·68	0·89
Oxygen (by difference).	1·43	2·44	1·90
	100·00	100·00	100·00

The hydrogen was probably present, at least to some extent, in th form of moisture taken up during cooling and weighing; charcoa especially of the light pulverulent character of that from carbon oxide, is far more hygroscopic than oxide of copper, which, as is well known, is very difficult to get perfectly free from hygroscopic moisture. The oxygen was necessarily present to some extent as moisture, the rest being probably in the form of occluded carbon oxide and dioxide; any occluded *air* would also be reckoned as oxygen in the above analyses.

In order to obtain the corrections for the amounts of gas evolved from these two samples of carbon on heating after pumping out all gases expelled in a Sprengel vacuum at the ordinary temperature, weighed quantities were placed in tubes with asbestos plugs, and treated exactly as the mixtures of carbon and metallic oxides subsequently examined. In about half an hour after first setting the pump at work, all gas capable of coming off at the ordinary temperature was expelled, no appreciable amount being collected during five minutes' action of the pump, the mercury clicking thoroughly. On then heating to 100° in boiling water a little gas was evolved; in a few minutes the vacuum became again perfect, no more gas being evolved in five minutes more. In the same way a further quantity

was obtained on heating to 360° in mercury vapour, the vacuum again becoming perfect in a few minutes. Similarly a little more gas was obtained on successively heating to about 420° and again to near 450°, these temperatures being deduced from the effect of heating in a bath of melted solder in which were inserted glass tubes of the same size and thickness as those employed for the carbon, containing fragments of pure zinc (melting point close upon 420°) and pure antimony (melting point close upon 450°). This mode of approximating to the temperature to which the tube was heated was found to be fairly reliable, and not subject to greater errors than any other method of determining the temperature that could be conveniently adopted (Siemen's electrical pyrometer was not tried, however).

In this way the following quantities of gas were obtained from each sample of carbon* reckoned in c.cs. at 0° and 760′ per gram of carbon:—

Range of temperature.	Gas collected. Sugar carbon.	Carbon from CO.
15° to 100°	0·70	1·00
100° to 360°	0·98	
360° to 420° (lead just melted)	0·10	0·20
420° to about 460° (somewhat above melting point of antimony)	0·60	3·00
	2·38	4·20

The following analyses were made of the total gas thus collected:—

* Another sample of carbon was prepared from carbon oxide by passing over pure ferric oxide (Specimen A), boiling the resulting mass with hydrochloric acid, washing, drying, and heating in hydrogen to redness (any iron compound not washed out), boiling again with hydrochloric acid, thoroughly washing, drying, and gently igniting. This was found to give off a rather smaller quantity of gas, possibly because the additional heating in hydrogen had rendered it somewhat less porous.

Range of temperature.	Gas collected per gram of carbon.
15° to 360°	0·60
360° to 420°	0·20
420° to about 480°	2·00
	2·80

This gas consisted of—

Carbon dioxide	71·02
Carbon oxide	21·01
Other gases	7·97
	100·00

This sample was not employed in any of the experiments described below.

	Sugar carbon.	Carbon from CO.
Carbon dioxide	48·2	28·6
Carbon oxide (absorbed by cuprous oxide)	43·4	33·3
Other gases	8·4	38·1
	100·0	100·0

3 decigrams of carbon and 6 of metallic oxide were employed in every observation, the temperature determinations being made precisely as above described. Just as with the carbon alone, a practically perfect vacuum was obtained after each further heating of the tube after a few minutes' working of the pump, until a temperature was attained when gas began to come off continuously; this temperature was then taken as the temperature of initial action; on repeating the experiments the results were never further from those previously obtained than might readily be due to the comparative roughness of the means of estimating the temperature adopted, whilst in most cases almost absolute agreement was noticed.

The following are the numerical results obtained (it being understood that in every instance the tube was pumped vacuous at the ordinary temperature before any heat was applied, and that the temperature was never raised above the particular limit assigned till long after a vacuum had been again established, *i.e.*, until the mercury clicked perfectly and no appreciable amount of gas was collected in five minutes; the temperature was judged to be 420° when the zinc in the companion tube was partially, but not wholly melted, and similarly at 450°, when the antimony was partly, but not entirely, melted; it was estimated at about 430° when the zinc was just thoroughly melted, and 440° when the temperature was rising and the antimony showed signs of incipient fusion; at 460° and upwards, when the antimony was thoroughly melted, the temperature still rising. In a few instances temperatures a little below 360° were obtained by a hot air-bath furnished with a thermometer as described in § 5. The volumes of the gases are all reduced to 0° and 760′.

Copper Oxides.

Carbon from Sugar.

	Specimen (A), Cupric Oxide.			Specimen (B).		
Range of temperature ..	15—360°	360—420°	360—450°	15—360°	360—420°	420—450°
Time of heating in minutes	30	15	30	30	15	15
Carbon dioxide collected	..	2·05	4·30	..	..	10·90
Other gases „ ..	..	0·05	0·10	..	..	0·10
Total gas collected.....	0·4	2·10	4·40	0·50	0·55	11·00
Gas due to occlusion	0·50	0·53	0·61	0·50	0·53	0·61
Gas produced from action of carbon on metallic oxide	Nil.	1·57	3·79	Nil.	Nil.	10·39

	(Specimen (C).			Cuprous Oxide.	
Range of temperature ..	15—360°	360—430°	430—460°	15—360°	360—420°
Time of heating in minutes	30	15	15	30	30
Carbon dioxide collected	..	..	7·90	—	12·30
Other gases „ ..	..	..	0·10	—	0·20
Total gas collected..	0·45	0·50	8·00	0·50	12·50
Gas due to occlusion....	0·50	0·53	0·61	0·50	0·61
Gas produced from action of carbon on metallic oxide.....	Nil.	Nil.	7·39	Nil.	11·89

Carbon from CO.

	Specimen (A).			Specimen (B).	
Range of temperature ..	15—300° (hot-air bath)	350—360° (hot-air bath)	360° (in mercury vapour)	15—360°	360—420°
Time of heating in minutes	30	30	30	30	15
Carbon dioxide collected	..	..	2·20	..	5·40
Other gases „ ..	..	..	0·10	..	0·10
Total gas collected.....	0·25	0·40	2·30	0·20	5·50
Gas due to occlusion	0·30	0·30	0·30	0·30	0·40
Gas produced by action of carbon on metallic oxide	Nil.	0·10	2·00	Nil.	5·10

University of Michigan

Carbon from CO.

	Specimen (C).			Cuprous Oxide.		
Range of temperature ..	15—360°	360—420°	420—440°	15—340° (hot-air bath)	340—350° (hot-air bath)	360° (in mercury vapour)
Time of heating in minutes	30	15	15	30	30	30
Carbon dioxide collected.	..	..	5·5	..	0·50	1·70
Other gases „ ..	..	..	0·1	..	0·10	0·10
Total gas collected.....	0·30	0·40	5·6	0·25	0·60	1·80
Gas due to occlusion....	0·30	0·36	About 1·0	0·30	0·30	0·30
Gas produced by action of carbon on metallic oxide	Nil.	Nil.	4·6	Nil.	0·30	1·50

FERRIC OXIDES.

Carbon from Sugar.

	Ferric Oxide (A).			
Range of temperature.....	15—360°	About 360° (in Hg vapour)	360—420°	420—480°
Time of heating in minutes	15	30	15	15
Carbon dioxide collected	..	..	..	2·90
Other gases „	..	..	..	0·10
Total gas collected	0·40	0·50	0·55	3·00
Gas due to occlusion	0·50	0·50	0·53	0·71
Gas produced from action of carbon on metallic oxide.....	Nil.	Nil.	Nil.	2·29

	Ferric Oxide (B).			
Range of temperature.....	15—360°	About 360° (in Hg vapour)	360—420°	420—480°
Time of heating in minutes	15	30	15	15
Carbon dioxide collected	..	..	..	2·60
Other gases „	..	..	..	0·10
Total gas collected	0·45	0·50	0·55	2·70
Gas due to occlusion	0·50	0·50	0·53	0·71
Gas produced from action of carbon on metallic oxide.....	Nil.	Nil.	Nil.	1·99

Carbon from Sugar.

	Ferric Oxide (C).			
Range of temperature	15—360°	About 360° (in Hg vapour)	360—420°	420—480°
Time of heating in minutes	15	30	15	15
Carbon dioxide collected	..	..	..	2·40
Other gases „	..	..	..	0·10
Total gas collected	0·40	0·50	0·60	2·50
Gas due to occlusion	0·50	0·50	0·53	0·71
Gas produced from action of carbon on metallic oxide.....	Nil.	Nil.	Nil.	1·79

Carbon from CO.

	Ferric Oxide (A).			
Range of temperature	15—360°	About 360° (in Hg vapour)	360—420°	420—440°
Time of heating in minutes	15	30	15	15
Carbon dioxide collected	..	..	..	2·50
Other gases „	..	..	..	0·20
Total gas collected	0·25	0·30	0·45	2·70
Gas due to occlusion	0·30	0·30	0·40	1·00
Gas produced from action of carbon on metallic oxide.....	Nil.	Nil.	Nil.	1·70

Ferric Oxide (B).

(Not determined, the specimen being entirely used up.)

	Ferric Oxide (C).			
Range of temperature.....	15—360°	About 360° (in Hg vapour)	360—420°	420—440°
Time of heating in minutes	15	30	15	15
Carbon dioxide collected	..	..	..	2·60
Other gases „	..	..	..	0·20
Total gas collected.....	0·20	0·30	0·40	2·80
Gas due to occlusion	0·30	0·30	0·40	1·00
Gas produced from action of carbon on metallic oxide.....	Nil.	Nil.	Nil.	1·80

From these observations the following values are deduced as the temperatures of initial actions:—

Copper Oxides.

	Specimen (A).	Specimen (B).	Specimen (C).	Cuprous oxide.
Sugar charcoal....	390°	430°	440°	390°
Carbon from CO ..	350	390	430	345

Iron Oxides.

	Specimen (A).	Specimen (B).	Specimen (C).
Sugar charcoal	450°	450°	450°
Carbon from CO.....	430	—	430

The above numbers indicate further how energetic is the action of carbon oxide on copper and iron oxides; the gas collected was always practically wholly carbon dioxide, indicating that all carbon oxide evolved from occlusion as well as any due to the action of carbon on carbon dioxide, or on the metallic oxide, was wholly oxidized by the metallic oxide.

An experiment was made by Lowthian Bell (*loc. cit.*, p. 53), which appears at first sight to indicate that an extremely intimate mixture of partially reduced ferric oxide and carbon, prepared by leading carbon oxide over heated ferric oxide, is capable of evolving gas at a temperature of 250—265°, and therefore that carbon begins to reduce this form of iron oxide at that temperature. One gram of the mixture was placed in a tube, air displaced by a current of nitrogen, and the tube sealed and heated in an air-bath for 4½ hours; at the end of that time, on opening the tube under mercury, it was found to contain about 7·0 c.cs. of carbon oxide and 0·16 of carbon dioxide. As the mixture contained carbon 52·14, iron 35·13, and oxygen 12·73 per cent., this amount of gas represents about 13·4 c.cs. of carbon oxide and 0·3 of carbon dioxide per gram of carbon.

Admitting that this gas was really formed by the action of the carbon on the partially reduced iron oxide, it would not in any way vitiate any conclusions drawn from the results above described, nor is it necessarily opposed to them in any way, since it is highly probable that the oxide of iron, partially reduced at about 400° by carbon oxide, would be excessively spongy and in an entirely different physical state from the ferric oxide examined by us, and therefore that action would commence at a lower temperature; but the following experiment renders it somewhat doubtful as to how far this gas really did arise from the action of the carbon on the iron oxide, and how far it was simply occluded gas displaced by the heating and not perfectly reabsorbed as the tube cooled. We prepared an analogous mixture containing—

Carbon	39·4
Metallic iron (soluble on digesting with iodine and boiled water)	23·3
Iron existing as oxide (insoluble in iodine water)	31·6
Oxygen (by difference)	5·7
	100·0

and then placed a gram of it in a tube, displaced all air by nitrogen, and exhausted cold with the Sprengel pump. After subtracting from the total bulk of gas collected that due to the capacity of the tube, &c., a residue of 1·2 c.cs. appeared, and on analysing the expelled gas just 1·2 c.cs. of carbon oxide were found, or 3·0 c.cs. per gram of carbon present, and not more than traces of carbon dioxide. On successively heating to 100°, to 250°, and to 360°, gas was pumped out at each heating, the tube speedily becoming practically vacuous till the temperature was again raised. The following quantities of gas were thus extracted, calculated per gram of carbon, so as to compare the figures with Lowthian Bell's results:—

	At ordinary temperatures.	15° to 100°.	100° to 250°.	250° to 360°.	Total.
Carbon dioxide..	Nil.	2·0	2·0	3·3	7·3
Carbon oxide....	3·0	0·5	traces.	0·5	4·0
					11·3

It is evident from the circumstance that carbon oxide was actually extracted at the ordinary temperature, that this gas, at any rate, must have been occluded; whilst the fitful expulsion of the remaining gas on raising the temperature by successive stages, renders it much more probable that the rest of the gas was also occluded than that it was due to the action of the carbon on the iron oxide. The gradually increasing amounts of carbon dioxide are doubtless due to the partial oxidation of the carbon oxide by the hot iron oxide. The much smaller amount of occlusion observed in the carbon experimented with by us as above described, is probably due simply to alteration of texture during the process of freeing from reduced iron, &c.

§ 7. Discussion of the above results.

It is abundantly manifest that the temperature of initial action of carbon oxide and of hydrogen on all the metallic oxides examined, varies considerably with the physical state of the metallic oxide; that of carbon varies not only with the physical state of the metallic oxide, but also with that of the carbon, a light pulverulent carbon beginning to act at a much lower temperature than a hard, dense, coke-like

charcoal, even though the latter be reduced to very fine powder. In the case of ferric oxide, although a difference in physical structure of the carbon produces a notable difference in temperature of initial action, yet no appreciable difference in temperature appears to be caused by any initial difference in the physical state of the ferric oxide, the reason for this presumably being that at a temperature of 400° and upwards the "precipitated" oxide alters its texture, and becomes in structure the same, or nearly the same, as that produced in the first instance by ignition processes. This alteration in physical texture by heat alone does not seem to take place, or at any rate not to so great an extent, with oxides of copper.

Nextly, on comparing the temperatures of initial action on a given kind of metallic oxide of different reducing agents, it is invariably found that *that reducing agent begins to act at the lowest temperature which has the greatest heat of combustion;* so that the heat disturbance during its reaction has (algebraically) the greatest value. Thus hydrogen always begins to act at a lower temperature than carbon, and carbon oxide at a lower temperature than hydrogen:—

	Carbon oxide.	Hydrogen.	Sugar carbon.	Carbon from CO.
Cupric oxide A....	60°	85°	390°	350°
„ B....	125	175	430	350
„ C....	146	172	440	430
Cuprous oxide	110	155	390	345
Ferric oxide A	202	260	450	430
„ B	90	195	450	—
„ C	220	245	450	430

Again, when cupric and ferric oxides, prepared by analogous processes, and, therefore, presumably in much the same physical state, are compared, it is uniformly found that the temperature of initial action of a given reducing agent *is lower on oxide of copper than on oxide of iron; i.e.*, that the action commences at a lower temperature the greater (algebraically) the value of the heat disturbance:—

Metallic Oxides prepared by precipitation.

	Carbon oxide.	Hydrogen.	Sugar carbon.	Carbon from CO.
Copper	60°	85°	390°	350°
Iron.....	90	195	450	430 ?*

Metallic Oxides prepared by ignition of Salts, &c.

Copper	125°	175°	430°	390°
Iron.....	202	260	450	430
	220	245	450	430

* Deduced from the results with the other specimens.

That this rule is not invariable for all metallic oxides has been already indicated (§ 1). It is noticeable that cuprous oxide, having much the same "heat of formation" as cupric oxide (§ 3, ii), and, therefore, causing much the same heat disturbance during its reduction by a given reducing agent, is uniformly first reduced at a temperature no further removed from the temperature of initial action on one or other form of cupric oxide than may readily be due to difference in physical state.

II.—*On the Influence exerted by Time and Mass in certain Reactions in which insoluble Salts are produced.*

By M. M. Pattison Muir, F.R.S.E., Prælector in Chemistry, Caius College, Cambridge.

1. If two salts can, by an interchange of acids and of bases, produce an insoluble compound, that insoluble compound is actually produced when solutions of the salts in question are mixed. The first action of the two salts upon one another results in the production of a small quantity of the insoluble compound, which is immediately removed, by precipitation, from the sphere of action; the original conditions being thus partially restored, a further quantity of the insoluble compound is produced, and this alternate maintenance and disturbance of equilibrium is carried on until the whole of the insoluble compound which can be produced has actually been produced.

2. In a paper published in 1857 (*Chem. Soc. J.*, ix, 54), Gladstone has shown that when two salts are mixed under circumstances such that all the resulting bodies are free to act and react, the proportions in which the various bases and acids enter into combination are partly dependent upon the mass of each substance in the mixture, and that "an alteration in the mass of any of the compounds present alters the amount of every one of the other compounds, and that in a regularly progressive ratio;" further, that this "equilibrium of affinities" is in certain cases not attained "for hours, or even days."

Now, although when an insoluble compound is produced, the equilibrium which was first established is destroyed by the removal of the new salt from the sphere of action; and, although the process of precipitation usually takes place with so much rapidity as to forbid any measurement of the time occupied, chemists, nevertheless, generally, I think, believe that the mass of the so-called precipitant influences the amount of the precipitate, and also the time during which the process

of precipitation proceeds. In a note to the paper referred to, Gladstone remarks: "It is easily conceivable that when the affinity for each other of the two substances which produce the insoluble compound is very weak, the action may last some time, and become evident to our senses. Is not this actually the case when . . . . carbonate of soda in solution is added to chloride of calcium?" &c.

3. In the following quantitative measurements of the influence of time in precipitation, and of mass of the precipitant on the amount of insoluble compound produced, I have availed myself of the suggestion made in the foregoing quotation from Gladstone's paper.

A solution of calcium chloride of known strength was prepared by dissolving a weighed quantity of pure calcspar in hydrochloric acid, evaporating repeatedly to dryness after successive additions of water, care being taken to avoid loss by spirting, and making up to a determinate volume. Solutions of pure potassium and sodium carbonates, of known strength, were also prepared. A certain volume of the carbonate solution was diluted with a fixed volume of water, a measured quantity of calcium chloride solution was run in, and the contents of the beaker were shaken up once; after standing for a fixed number of minutes the precipitate was collected, washed, and dissolved in a measured volume of standard hydrochloric acid, the liquid was boiled to expel carbon dioxide, and, after cooling, the excess of acid was determined by means of half-normal ammonia solution.

The results can only be regarded as approximate; nevertheless, for the object which I set before myself, they are, I think, almost as instructive as if their perfect accuracy were unimpeachable.

The circumstances preventing great exactness in the results, are, principally, the fact that the process of filtration occupied an appreciable time, usually five to six minutes, and the fact that calcium carbonate is slightly soluble in water. The inaccuracy introduced by the first circumstance attaches equally to all the experiments, inasmuch as the volume of liquid to be filtered was in each case the same, and the actual duration of the process of filtration did not vary more than one minute. The amount of wash water employed was also approximately the same in each case, hence the inaccuracy arising from the second circumstance mentioned above also attaches equally to all the experiments. The actual amount of calcium carbonate dissolved could not in any case cause a greater error than 1 per cent. on the final result.

The results are, I think, strictly comparable among themselves, and the absolute errors are not considerable.

4. I will first consider the influence of time:—

Table I.

Total volume of liquid = 70 c.c.

10 c.c. $CaCl_2$ solution = 107·062 mgm. $CaCl_2$. 14 c.c. Na_2CO_3 solution.

Proportion $CaCl_2$: Na_2CO_3 : : 1 : 1 molecule.

Time.	Percentage of $CaCO_3$ produced, calculated on total theoretical yield.
5 minutes.	74·53
30 ,,	84·68
60 ,,	85·91
180 ,,	93·17
46 hours.	94·27

Table II.

10 c.c. $CaCl_2$ solution. 28 c.c. Na_2CO_3 solution.

Na_2CO_3 : $CaCl_2$: : 2 : 1 molecule. Volume = 70 c.c.

Time.	Percentage of $CaCO_3$ produced.
5 minutes.	92·08
30 ,,	93·17
60 ,,	94·27
180 ,	100·00

Table III.

10 c.c. $CaCl_2$ solution. 42 c.c. Na_2CO_3 solution.

Na_2CO_3 : $CaCl_2$: : 3 : 1 molecule. Volume = 70 c.c.

Time.	Percentage of $CaCO_3$ produced.
5 minutes.	94·27
30 ,,	95·37
60 ,,	96·87
180 ,,	100·00

Table IV.

10 c.c. $CaCl_2$ solution. 56 c.c. Na_2CO_3 solution.

Na_2CO_3 : $CaCl_2$: : 4 : 1 molecule. Volume = 70 c.c.

Time.	Percentage of $CaCO_3$ produced.
5 minutes.	100·00

Table V.

10 c.c. $CaCl_2$ solution. 19·5 cc. K_2CO_3 solution.

K_2CO_3 : $CaCl_2$: : 1 : 1 molecule. Volume = 70 c.c.

Time.	Percentage of $CaCO_3$ produced.
5 minutes.	81·11
30 ,,	85·00
60 ,,	85·91
180 ,,	94·27
46 hours.	94·27

Table VI.

10 c.c. $CaCl_2$ solution. 39 c.c. K_2CO_3 solution.
$K_2CO_3 : CaCl_2 :: 2 : 1$ molecule. Volume = 70 c.c.

Time.	Percentage of $CaCO_3$ produced.
5 minutes.	94·27
30 ,,	98·65
60 ,,	100·00

Table VII.

10 c.c. $CaCl_2$ solution. 58·5 c.c. K_2CO_3 solution.
$K_2CO_3 : CaCl_2 :: 3 : 1$ molecule. Volume = 70 c.c.

Time.	Percentage of $CaCO_3$ produced.
5 minutes.	96·45
30 ,,	98·65
60 ,,	100·00

Table VIII.

10 c.c. $CaCl_2$ solution = 57·045 mgm. $CaCl_2$. 40·9 c.c. K_2CO_3 solution.
$K_2CO_3 : CaCl_2 :: 4 : 1$ molecule. Volume = 70 c.c.

Time.	Percentage of $CaCO_3$ produced.
5 minutes.	100·00

The results contained in Tables I and II are represented graphically by curves C and D respectively: the results in Tables V and VI by curves A and B respectively.

It is evident that the greater portion of the chemical change is produced during the first five minutes of the action; after the expiry of that time the action very much decreases in rapidity; the amount of change in the next 25 to 30 minutes is, however, always greater than the amount accomplished in the second period of the same duration. The action proceeds, as it were, with a rush at first; it then gradually becomes more and more slow.

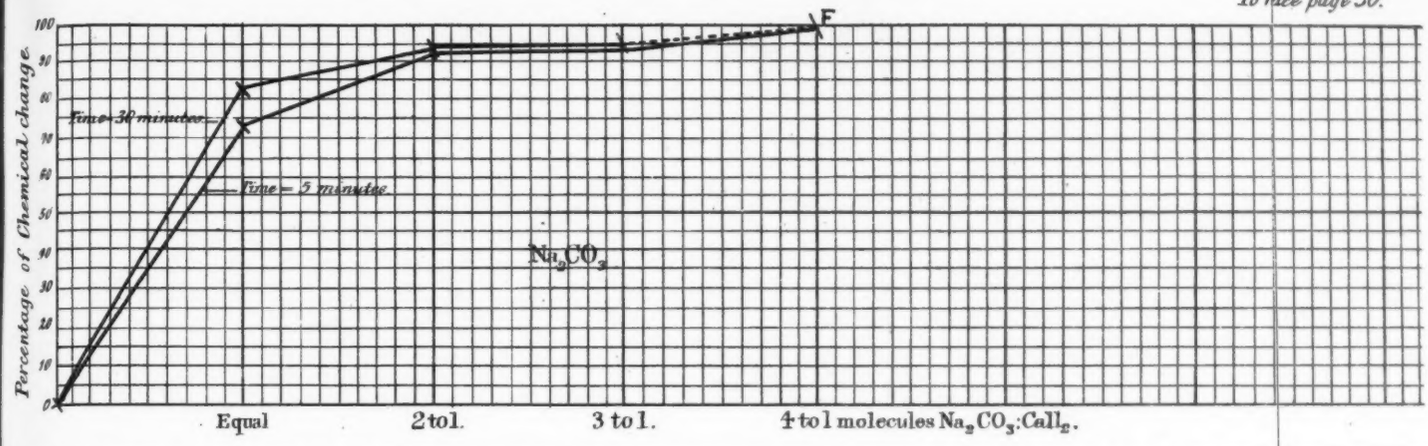
5. The numbers obtained also illustrate the influence exerted by increasing the mass of one of the salts. This influence will be rendered more apparent by arranging the numbers in a somewhat different form:—

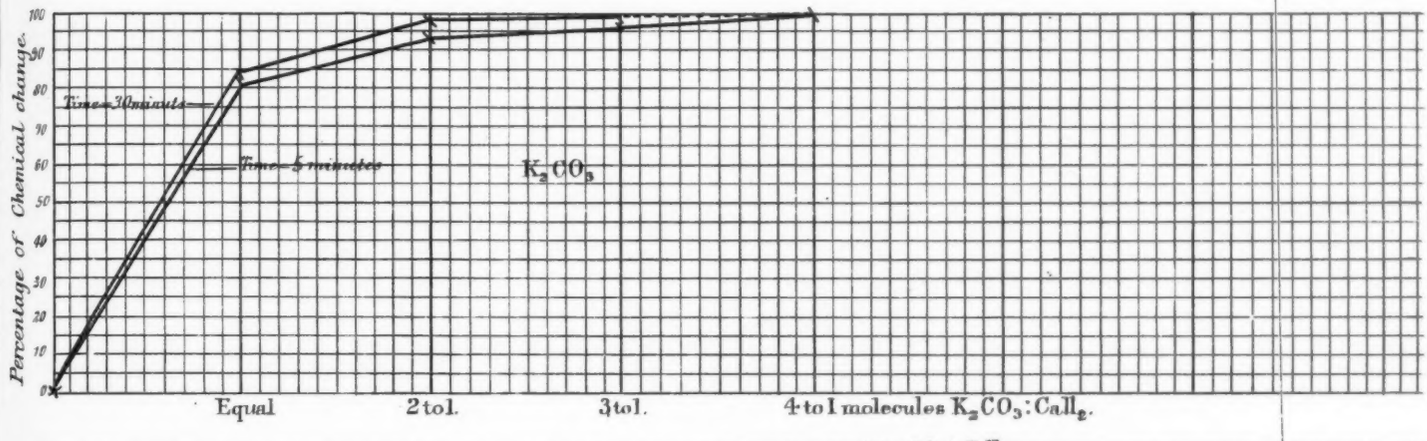
Table IX.

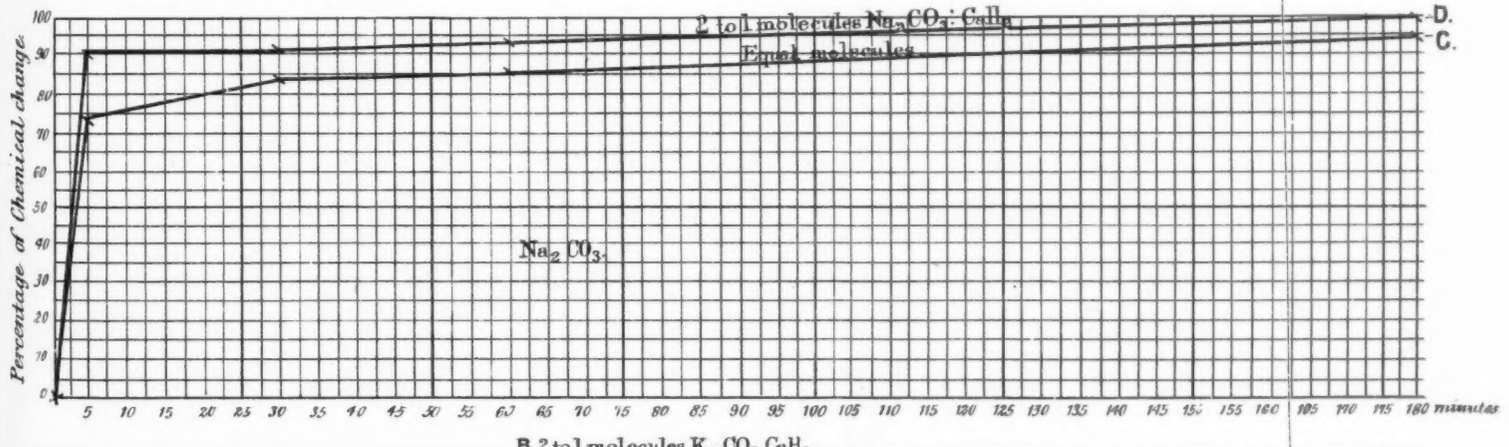
Details as before.
Time = 5 minutes.

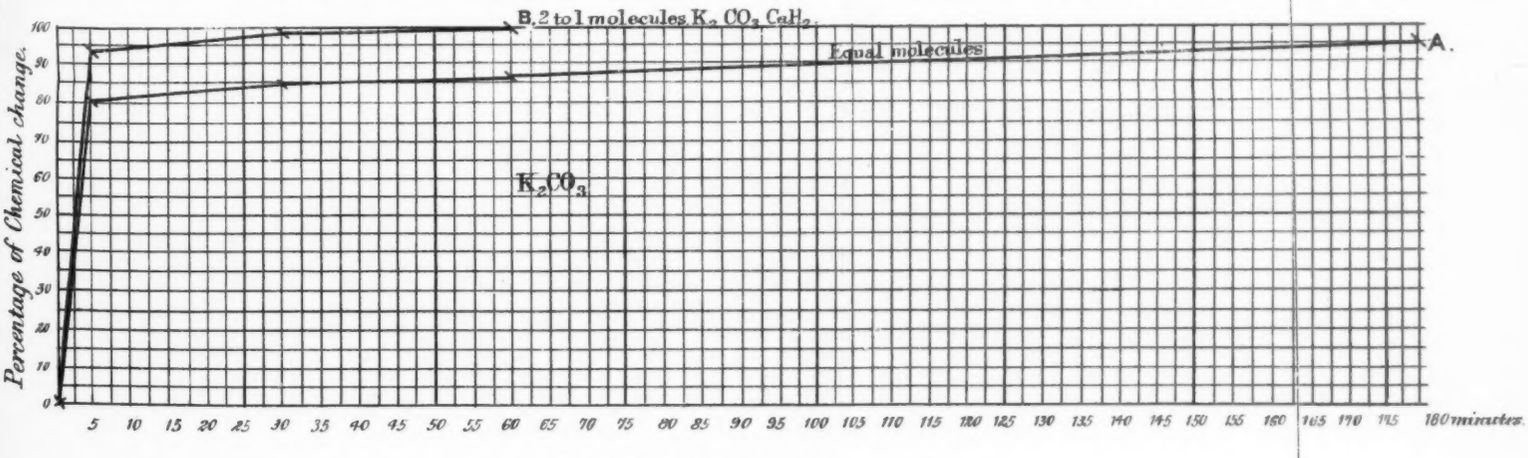
$Na_2CO_3 : CaCl_2$.	Percentage of $CaCO_3$ produced.
1 : 1 mol.	74·53
2 : 1 do.	92·08
3 : 1 do.	94·27
4 : 1 do.	100·00

To face page 30.









Harrison & Sons, Lith. 3 Martins Lane, W.C.

Time = 30 minutes.	
1 : 1 mol.	85·00
2 : 1 do.	93·17
3 : 1 do.	95·37
4 : 1 do.	100·00
Time = 60 minutes.	
1 : 1 do.	85·91
2 : 1 do.	94·27
3 : 1 do.	96·87
4 : 1 do.	100·00
Time = 180 minutes.	
1 : 1 do.	93·17
2 : 1 do.	100·00
Time = 46 hours.	
1 : 1 do.	94·27
2 : 1 do.	100·00

Table X.

Details as before.

Time = 5 minutes.

K_2CO_3 : $CaCl_2$.	Percentage of $CaCO_3$ produced.
1 : 1 mol.	81·11
2 : 1 do.	94·27
3 : 1 do.	96·45
4 : 1 do.	100·00
Time = 30 minutes.	
1 : 1 do.	84·68
2 : 1 do.	98·65
3 : 1 do.	98·65
4 : 1 do.	100·00
Time = 60 minutes.	
1 : 1 do.	85·91
2 : 1 do.	100·00
Time = 180 minutes.	
1 : 1 do.	94·27
2 : 1 do.	100·00
Time = 46 hours.	
1 : 1 do.	94·27
2 : 1 do.	100·00

The first two sections of Table IX are represented graphically in the curves marked F ; the first two sections of Table X are represented in the curves marked E.

University of Michigan

6. These numbers show that the equation—

$$CaCl_2 + M_2CO_3 = 2MCl + CaCO_3,$$

does not furnish a full expression of the action of sodium or potassium carbonate upon calcium chloride. When the two salts are mixed in the proportion expressed by their respective formulæ, the action represented in the equation is not completed, even after the expiry of so long a time as 46 hours. In order fully to realise the equation, the mass of the alkaline carbonate must exceed that which would be actually required to transform the whole of the calcium chloride into carbonate were the equation strictly true. When two molecules of potassium carbonate are present to one molecule of calcium chloride, the action is complete after the lapse of an hour; were sodium carbonate employed, it would be necessary to use rather more than three molecules for one of the alkaline earth chloride, in order to complete the action in the same period of time. If the mass of the alkaline carbonate be four times that represented in the equation, the action is complete in five minutes.

7. So soon as the solutions are mixed an atomic interchange begins, resulting, we must believe, in the formation of calcium carbonate, which, being insoluble, is at once removed from the sphere of action, and of sodium or potassium chloride, while at the same time portions of sodium or potassium carbonate and of calcium chloride remain undecomposed. As the mass of sodium or potassium chloride increases, the action of the small residual portions of sodium or potassium carbonate upon the remaining calcium chloride becomes slower and slower, until it finally ceases.

It may, perhaps, be allowable to imagine the few calcium chloride and sodium or potassium carbonate molecules as so widely separated from one another by the great mass of sodium chloride molecules, that among their excursions to and fro they rarely, if ever, come into collision with one another. The addition of a further quantity of the sodium or potassium carbonate molecules of course increases the chances in favour of any one of these molecules meeting with a molecule of calcium chloride, and hence the chances in favour of the production of fresh quantities of calcium carbonate. Again, it is not improbable that a secondary reaction may take place to a limited extent, represented by such an equation as—

$$(1.)\ CaCO_3 + 2MCl = CaCl_2 + M_2CO_3.$$

If this reaction does take place we should expect that so soon as the M_2CO_3 produced reaches a certain amount, the converse reaction—

$$(2.)\ CaCl_2 + M_2CO_3 = CaCO_3 + 2MCl$$

would again begin, and that these two reactions would maintain the composition of the mixture constant. But if we increase the mass of

M_2CO_3, it is clear that the second reaction will preponderate over the first, and if we ensure that when the second reaction is finished, a considerable number of M_2CO_3 molecules remain unacted upon, the conditions under which reaction (1) can be realised will no longer prevail.

8. Increasing the mass of the individual molecules of the precipitant tends to increase the amount of chemical change brought about in a stated period of time.

The molecular weights of sodium and potassium carbonates (supposing the ordinary formulæ to be really molecular formulæ) are to one another as 53 is to 69·1. The numbers obtained show that when potassium carbonate is used, a larger quantity of calcium carbonate is formed in a given time than when sodium carbonate is employed, except when the action is allowed to proceed during very extended periods. After 46 hours the amount of calcium carbonate formed by the action of sodium carbonate was the same as that produced by the action of potassium carbonate. In the following table I have arranged the numbers so as to illustrate the point under consideration.

Table XI.

Details as before.

	Percentage of $CaCO_3$ produced.			
	Time = 5 minutes.		Time = 30 minutes.	
Proportion of $M_2CO_3 : CaCl_2$.	Na_2CO_3.	K_2CO_3.	Na_2CO_3.	K_2CO_3.
1 : 1 mol.	74·53	81·11	84·68	85·00
2 : 1 „	92·08	94·27	93·17	98·65
3 : 1 „	94·27	96·45	95·37	98·65
4 : 1 „	100·00	100·00	100·00	100·00
	Time = 60 minutes.		Time = 180 minutes.	
1 : 1 „	85·91	85·91	93·17	94·27
2 : 1 „	94·27	100·00	100·00	100·00
3 : 1 „	96·87	100·00		
4 : 1 „	100·00	100·00		
	Time = 46 hours.			
1 : 1 „	94·27	94·27		

9. If the hypothesis put forward in paragraph 7 be correct, it is evident that any circumstances which would increase the excursions of the residual molecules of sodium or potassium carbonate and of calcium chloride, would also increase the chances in favour of collision occurring between these molecules, and hence the chances in favour of the production of larger quantities of insoluble calcium carbonate. On the other hand, any circumstances tending to decrease the excursions of

these residual molecules, or tending to increase the number of molecules which take no part in the production of calcium carbonate, and hence to decrease the chances of the sodium or potassium carbonate and the calcium chloride molecules coming into collision, would also tend to diminish the amount of calcium carbonate produced. Raising the temperature at which the two salts are allowed to react upon one another would tend to increase the number of excursions of the different molecules; diluting the solutions would tend to decrease the chances of collision between the two sets of molecules.

I have carried out a few experiments under each of these conditions. The experiments already detailed were performed at the ordinary temperature, viz., 15° to 20°.

Table XII.

Details as before.

Time = 5 minutes. Temperature = 40°.

	Percentage of calcium carbonate produced.	
$M_2CO_3 : CaCl_2$.	Na_2CO_3.	K_2CO_3.
1 : 1 mol.	88·50	85·50
2 : 1 „	93·17	95·36
3 : 1 „	96·45	96·45
4 : 1 „	100·00	100·00

Table XIII.

Details as before.

Volume = 140 c.c.

	Percentage of calcium carbonate produced.			
	Time = 5 minutes.		Time = 30 minutes.	Time = 60 minutes.
$M_2CO_3 : CaCl_2$.	Na_2CO_3.	K_2CO_3.	Na_2CO_3.	Na_2CO_3.
1 : 1 mol.	63·58	63·58	74·05	75·64
2 : 1 „	78·92	87·69	86·84	86·84
3 : 1 „	86·84	—	88·25	91·05

Increase of temperature causes in every case an increase in the amount of calcium carbonate produced. Dilution causes a very marked decrease. A small proportion of this decrease may be traced to the solvent action of the larger volume of water upon the calcium carbonate precipitated; but there can be no doubt that dilution, apart altogether from the solvent action of the diluent upon the precipitate, very materially decreases the amount of chemical change taking place in a definite interval of time.

10. If sodium or potassium chloride were employed as diluent in

place of water, we should expect to find a marked decrease in the amount of calcium carbonate formed, inasmuch as the alkaline chloride would not only act as a diluent, but it would also tend to increase the action represented in equation (1) in paragraph 7. The following table contains the results of some experiments performed with the view of testing the reasonableness of this expectation.

Table XIV.

10 c.c. $CaCl_2$ solution, with 16, 32, and 48 c.c. K_2CO_3 solution : volume made up to 70 c.c. with dilute NaCl solution (1 c.c. = 8·5 mgm. NaCl).

	Percentage of $CaCO_3$ produced.	
$M_2CO_3 : CaCl_2$.	Time = 5 minutes.	Time = 30 minutes.
1 : 1 mol.	64·43	64·43
2 : 1 „	84·05	92·44
3 : 1 „	92·44	95·24

It is well known that alkaline chlorides exert a solvent action upon calcium carbonate; but the decrease in the amount of calcium carbonate produced in these experiments as compared with that formed in experiments where water alone was employed as diluent, cannot be entirely traced to such an action. The alkaline chloride appears rather to prevent the formation of calcium carbonate. Even were we to regard the action of the chloride as that of a solvent, we must surely believe that the calcium carbonate is transformed into chloride, and passes into solution in this form.

11. It occurred to me that discontinuous addition of one of the solutions would probably bring about the production of larger quantities of calcium carbonate than are found when the whole of one solution is added to the whole of the other at one time. A few experiments were tried; the results are summarised as follows :—

Table XV.

Details as before.

$CaCl_2$ solution added in small successive portions during 3½ minutes; liquid shaken up after each addition; whole allowed to remain at rest during 1½ minutes after final addition of calcium chloride.

	Percentage of $CaCO_3$ produced.	
$M_2CO_3 : CaCl_2$.	Na_2CO_3.	K_2CO_3.
1 : 1 mol.	89·00	89·65
2 : 1 „	100·00	100·00

$CaCl_2$ solution added in small successive quantities during 20 minutes, whole allowed to remain at rest during additional 10 minutes.

	Na_2CO_3.	K_2CO_3.
1 : 1 mol.	94·27	94·27
2 : 1 do.	100·00	100·00

$CaCl_2$ solution added in small successive quantities during 150 minutes, whole allowed to remain at rest during additional 30 minutes.

	Na_2CO_3.	K_2CO_3.
1 : 1 mol.	94·27	94·27
2 : 1 do.	100·00	100·00

These results show that when one of the reacting solutions is added discontinuously, the action reaches a maximum more quickly than when the solutions are mixed at one time, but that the maximum so reached is no greater than that which is finally attained under the latter conditions.

12. I have also carried out a few experiments using ammonium, sodium, and potassium oxalates as precipitants, and determining the amount of calcium oxalate produced by dissolving in warm sulphuric acid and titrating with potassium permanganate. The results are not, however, of much interest, as the action of time and of mass is not so marked as in those experiments which have been already detailed. The chemical change is much sooner completed when oxalates than when carbonates are employed as precipitants. I give the results of my experiments so far as they have been pursued.

Table XVI.

20 c.c. $CaCl_2$ solution = 114·09 mgm. Volume = 70 c.c.
Temperature = 15° to 20°. Time = 5 minutes.

	Percentage of CaC_2O_4 produced.		
$M_2C_2O_4 : CaCl_2$.	$(NH_4)_2C_2O_4$.	$Na_2C_2O_4$.	$K_2C_2O_4$.
1 : 1 mol.	93·85	93·85	93·85
2 : 1 do.	100·00	100·00	100·00
3 : 1 do.	100·00	100·00	100·00

13. In a paper entitled "On the Application of Liquid Diffusion to produce Decompositions" (*Chem. Soc. J.*, iii, 60), Graham describes certain experiments from which "it follows that cold solutions of sulphate of lime and chloride of sodium may be mixed without decomposition, or without any sensible formation of sulphate of soda." Graham further remarks, that "it would be interesting to submit such a mixture to a diffusion experiment after being kept for different periods. The effects of time and temperature are so often convertible that we might anticipate a gradual formation of sulphate of soda."

I have carried out Graham's idea in a somewhat modified form.

Although the results of the experiments to be now described cannot strictly be brought under the heading of the present paper, inasmuch as no insoluble salt is produced in the reaction, nevertheless, as the results illustrate the influence of time and mass, and are also interesting from another point of view, I venture to detail them.

Solutions of calcium sulphate and sodium chloride were mixed and allowed to remain in covered beakers during four weeks. Measured portions were then withdrawn, and to each a volume of alcohol, fully equal to the volume of the liquid itself, was added. The precipitated calcium sulphate was collected, washed with alcohol, ignited, and weighed. An equal volume of the calcium sulphate solution was treated with alcohol in the same way, and the calcium sulphate contained therein was thus determined.

The results are contained in the following table:—

Table XVII.

(1.) 100 c.c. $CaSO_4$ solution = 191·0 mgm. $CaSO_4$ + 10 c.c. NaCl solution = 233·3 mgm. NaCl.

Amount of $CaSO_4$ in solution after 28 days = 167·0 mgm.

(2.) 100 c.c. $CaSO_4$ solution + 50 c.c. NaCl solution.

Amount of $CaSO_4$ in solution after 28 days = 103·0 mgm.

(3.) 100 c.c. $CaSO_4$ + 100 c.c. NaCl solution.

Amount of $CaSO_4$ in solution after 28 days = 64·0 mgm.

A very considerable decomposition of the calcium sulphate by the sodium chloride had evidently taken place.

If the results be arranged in the form adopted in many of the preceding tables, the influence of mass on the amount of chemical change becomes more apparent.

Temperature = ordinary. Time = 28 days.

$CaSO_4$: NaCl.	
1 : 1·42 mols.	Amount of $CaSO_4$ decomposed = 3·80 per cent. of the total $CaSO_4$ present.
1 : 7·1 mols.	Amount of $CaSO_4$ decomposed = 19·15 per cent.
1 : 14·2 mols.	Amount of $CaSO_4$ decomposed = 32·98 per cent.

The amount of chemical change varies almost directly with the mass of the sodium chloride employed.

I intend to carry out a series of experiments upon the influence of time and mass in bringing about the change under consideration, and hope to communicate the results to the Society at no distant date.

Graham's experiments show that on heating a mixture of calcium sulphate and sodium chloride, sodium sulphate is formed, and continues to exist in the cold solution.

The experiments detailed above show that a similar formation of sodium sulphate occurs, without heating, if solutions of the two salts be allowed to react upon one another for several weeks.

The secondary consideration which lends interest to these experiments may be stated in Graham's words: "If such formation of sodium sulphate be the case, we have an agency in the soil by which the alkaline carbonates required by plants may be formed from the chlorides of potassium and sodium, as well as from the sulphates of potash and soda: for the sulphate of lime generally present will convert these chlorides into sulphates."

This observation derives its force from the facts demonstrated by Graham, that sulphates of potassium and sodium are decomposed by lime-water, yielding diffusates which contain caustic potash and caustic soda respectively, but that chlorides of potassium and sodium are not so decomposed.

III.—*The Chemistry of Cocoa Butter.* Part I. *Two New Fatty Acids.*

By Charles T. Kingzett.

Some few months ago I commenced, at the suggestion of my friend, Dr. B. H. Paul, an investigation upon the chemistry of cocoa butter, and although my work has had many interruptions, some interesting and important results have been attained; so important indeed have been these results, that I am induced to publish this paper, which otherwise must be regarded as of a preliminary nature.

The sample of cocoa butter upon which I worked was obtained from Messrs. Cadbury and Sons. It was a hard, imperfectly transparent, slightly yellowish solid, melting at about 30° C., and when once melted, retaining the liquid state for some time at a temperature below that just mentioned. To alcohol of 85 per cent. and maintained at the boiling point, it gave up but traces of soluble matter, and from the fact that hot ammonia water extracted from it but traces of matter, I conclude that it is practically or entirely free from fatty acids, as such.

It was proved by special experiments to be also entirely free from volatile or soluble fatty acids.

1*st Experiment.*—40 grams were saponified by caustic soda solution, the mixture nearly neutralised with dilute sulphuric acid, and the precipitate of sodium salt washed after filtration. It was dissolved in much boiling water, and was then precipitated by barium chloride solution.

An attempt was made to estimate the oleate of barium contained in this salt, by extraction with boiling alcohol; but that employed (of 85 per cent.) dissolved some considerable quantity of a barium salt other than the oleate, whose free acid was solid at ordinary temperatures. I also attempted to estimate the oleic acid by converting the barium salt into lead salt, and extracting this by ether, but in course of the extraction the salt became yellow, and something more than mere oleate of lead dissolved.

The lead precipitate insoluble in ether was reconverted into barium salt, through the intervention of an ammonium soap made from the free acids and the barium salt analysed—

(1.) 0·495 grm. dry at 100° C. gave 1 048 grm. CO_2, and 0·427 grm. H_2O.

(2.) 0·4190 grm. gave 0·1490 $BaSo_4$.

Synopsis of Analysis:—

C.....	57·74
H.....	9·58
Ba	20·90
O.....	11·78

If we deduct the barium we get by calculation the following percentages for the free acid:—

C.....	73·00
H.....	12·11
O.....	14·89

The barium salt was now decomposed by hydrochloric acid in presence of ether, and the free acids obtained by distillation of the ether were recrystallised from alcohol. The first crop was lost; the second, which was evidently impure (being slightly coloured), was analysed; 0·212 grm. gave 0·545 grm. CO_2 and ·237 grm. H_2O.

C.....	70·11
H.....	12·42
O	17·47

2nd Experiment.—Another quantity of cocoa butter was now saponified and the sodium salt made into barium salt. This was decomposed by hydrochloric acid in presence of ether, and the fatty acids obtained by distillation of the ethereal solution crystallised from 85 per cent. alcohol containing animal charcoal in suspension; the last mother-liquor was retained.

The solid acid obtained, as described, was a snow-white powdery substance when dry.

It was recrystallised from alcohol, two successive crops being obtained; the first by deposition; the second after concentration.

The first crop had a melting point of 65°.

(*a.*) 0·164 grm. dried at 100° C., and burnt with $PbCrO_4$, with the aid of $KClO_3$, gave 0·197 grm. H_2O and 0·464 grm. CO_2.

(*b.*) 0·125 grm. gave 0·147 grm. H_2O and 0·353 grm. CO_2.

Synopsis:—

	a.	*b.*
C.....	77·16	77·01
H	13·35	13·06
O	9·49	9·93

This same mixture of acids (for such it eventually proved to be) was afterwards fractionated by recrystallisation from spirit into three portions, 1, 2, and 3, which were analysed.

Fraction 1. Melted at 68°.

(*a.*) 0·185 grm. gave 0·223 grm. H_2O, and 0·521 grm. CO_2.

(*b.*) 0·159 grm. gave 0·188 grm. H_2O.

C.....	76·81
H.....	13·35 and 13·14.
O.....	9·84

Fraction 2. Melted at 61°.

0·138 grm. gave 0·3960 CO_2 and 0·162 H_2O.

C.....	78·26
H.....	13·04
O.....	8·70

Fraction 3. Melted at 58°.

0·157 grm. gave 0·410 grm. CO_2, and 0·182 H_2O.

C.....	71·22
H.....	12·87
O.....	15·91

The second crop (following that which furnished these three fractions) was fractionated into two portions, each melting at 58°.

The oleic acid contained in cocoa butter was isolated from the last mother-liquor alluded to above, and obtained after these successive crops of solid fatty acids. It was made into ammonium salt, and this into barium salt, which was dried and extracted by alcohol. The powder thus obtained on cooling of the alcoholic extract was snow-white.

0·322 gave 0·105 $BaSO_4$ = 19·25 per cent. Ba.

Inasmuch as oleate of barium gives 19·59 per cent. Ba, and further seeing this acid had also the other properties of ordinary oleic acid, there is no reasonable doubt left regarding its true nature.

3rd Experiment.—Another quantity of cocoa butter was now saponified; the sodium soap washed slightly, and decomposed by sul-

phuric acid; the free acids were washed by repeated meltings with hot water, then dried and weighed. Weight = 37 grms.

It was recrystallised from alcohol in the presence of charcoal, and the mother-liquors treated as described below.

Four successive crops of fatty acids were obtained: (*a*) shortly after cooling to some extent; (*b*) on standing; (*c*) by concentration of mother-liquor; (*d*) after last fraction on standing. The first crop was further fractionated by alcohol into three portions, and the third crop into two portions; the mother-liquors being for the time disregarded.

Examination of the three fractions from first crop:—

(1.) Melted at 70·5°.

(2.) Melted at 70·8°.

(3.) Melted at 61·0°.

The first portion melting at 70·5° C. was again fractionated with two crops.

(*a.*) Melting at 71—71·5° C., and (*b*) melting at 71—71·5° C.

Analysis of (*a*):—

0·179 grm. gave 0·518 CO_2, and 0·219 H_2O.

C.....	78·92
H.....	13·59
O.....	7·49

This product was eventually further fractionated into two portions, the first of which was analysed.

It melted at 72·2°, solidified again at 69°.

(*a.*) 0·170 grm. gave 0·515 CO_2 and 0·213 H_2O.

(*b.*) 0·069 „ 0·208 „ „ 0·088 „

(*a.*)	(*b.*)
C. 82·62	82·21.
H. 13·92	14·16.
O. 3·46	3·63.

The second crop melted at 66° C.

The third crop melted at 56·5° C.

This last crop was further fractionated into two portions and a mother-liquor.

Portion (*a*) melted at 59 to 59·5° C., and (*b*) at 57·5 to 58° C.

Analysis of (*b*):—

0·204 grm. gave 0·542 CO_2 and 0·257 H_2O.

C.....	72·46
H.....	13·99
O.....	13·55

To recapitulate, we may here show in tabular form the percentage composition and melting points of the foregoing products:—

1.	2.	3.	4.	5.	6.	7.	8.	9.
M. p... 57—58°	58·5°	57·5°	—	68°	65°	61°	71·5°	72·2
C .... 70·11	71·22	72·46	73·00	76·81	77·16	78·26	78·92	82·62
H .... 12·42	12·87	13·99	12·11	13·14	13·06	13·04	13·59	13·92
O .... 17·47	15·91	13·55	14·89	10·05	9·88	8·70	7·49	3·46

Neglecting the intermediate terms, and taking the extremes reacted by the method employed, these latter are tolerably well represented by the formulæ, $C_{12}H_{24}O_2$ and $C_{64}H_{128}O_2$:—

	$C_{12}H_{24}O_2$.	$C_{64}H_{128}O_2$.
C	72·00	82·75
H	12·00	13·79
O	16·00	3·46
	100·00	100·00

Now of the products whose analyses are described above, only one was at all coloured, and that was the one containing 70·11 per cent.; moreover, this was the only one which was burnt with $PbCrO_4$ without the supplemental aid of potassic perchlorate, therefore, neglecting this, the nearest analyses approaching those just given are—

	$C_{12}H_{24}O_2$.		$C_{64}H_{128}O_2$.
C	71·22		82·62
H	12·87	and	13·92
O	15·91		3·46
	100·00		100·00

$C_{12}H_{24}O_2$ is the formula of lauric acid, which, however, has a melting point of 43°. As the lowest melting point I have yet observed among the fatty acids from cocoa butter is 57·5°, the fatty acid to which it belongs, if lauric acid, must contain some quantity of an acid of higher melting point than lauric acid. Therefore, the acid itself would be lower in the series $C_nH_{2n}O_2$ than lauric acid.

Further, the highest acid previously known in the series $C_nH_{2n}O_2$, is melissic acid, $C_{30}H_{60}O_2$, and whereas I have described a definitely crystalline substance of the empiric formula $C_{64}H_{128}O_2$, it is by far the highest acid term in the series, yet discovered.

But I would not claim to have attained as yet the ultimate limits in either direction; the higher acid may contain more than 64 atoms of carbon to the molecule, and the lower one may contain less than 12 atoms to the molecule. I have, however, exhausted the capabilities of the only process yet used by me; in the future, I intend to apply whatever other methods are available among those known, or in my power to devise.

It only remains for me to add that I have prepared barium, calcium, and silver salts of the higher acid, but refrain from publishing their percentage composition until more ultimate possibilities may have been attained. I may mention, however, that the silver salt is coloured only slightly by light, and is deposited by precipitation from an ammoniacal solution by argentic nitrate as a gelatinous mass, which, when dry, is highly electric and quite insoluble in alcohol of 85 per cent. and in ether. The higher fatty acid itself also appears to be somewhat electric; it crystallises in granules from a concentrated alcoholic solution, but in microscopic needles from a more dilute solution. At high temperatures it distils apparently unchanged. The crystalline character of the lower acid is more distinct, and sometimes it is obtained in beautiful pearly plates, and at others in fine long needles.

In the third experiment I determined, approximately, the amount of oleic acid contained in the 37 grams of total fatty acids from cocoa butter, by separating, as far as could be, all crystallisable solid fatty acids from the ultimate mother-liquors after recrystallisation. It amounted to about 20 per cent. of the total.

So far as I have ascertained, and merely for the sake of a calculation, it may be stated that a compound glyceride of the composition

$$C_3H_5\begin{cases}C_{12}H_{23}O_2\\C_{64}H_{127}O_2\\C_{18}H_{33}O_2\end{cases}$$

requires exactly 20 per cent. oleic acid to be furnished by the total acids derivable from it.

At the same time, it may be that cocoa butter is a mixture of the three glycerides, or even of more, whose fatty acids in such case form part of the intermediate crops not yet analysed.

Before concluding the paper, it should be stated that I have in vain searched chemical literature with the view of discovering any publication bearing upon my subject. But the only matter I have been able to find is a statement made in nearly all works to the effect that cocoa butter yields almost exclusively stearic acid, and the evidence of its purity when prepared is a permanent melting point of 69 to 70° C. It appears, therefore, that the melting point has hitherto been accepted as sufficient evidence of the presence of stearic acid; but, as will be seen from my investigation, this is entirely incorrect. Compared with the formula of the highest product I have obtained from cocoa butter, the melting point of 72·2° appears to be low, but it is impossible that the acid can contain less than 64 atoms of carbon, and should its melting point be regarded in any way as a difficulty, the acid could, of necessity only, be still higher in the series than so far ascertained. Without waiting until its molecular weight shall have been definitely

established, I propose for it the name of *Theobromic acid*, which recalls the source from which it is obtained, namely, the fat of the seeds of *Theobroma Cacao*. The seeds are known to yield from 30 to 50 per cent. of this fat.

IV.—*On Nitrification.*

By Robert Warington.

I have the pleasure of submitting to the Society a report of some experiments on nitrification recently carried out in the Rothamsted Laboratory.

The formation of nitrates in soil, under favourable conditions as to moisture, temperature, and aëration, is a reaction well known and frequently studied. It is a process of great technical importance, being the only natural source of saltpetre. It is also of the highest interest to the scientific agriculturalist, nitrates being invaluable as plant-food, and their loss by drainage one of the most serious difficulties with which a farmer has to contend.

The bodies yielding nitric acid in the soil are, firstly, the various nitrogenous organic substances which arise from the decay of vegetable or animal matter; and secondly, ammonium salts, either produced in small quantity during the decay of organic matter, or carried to the soil by rain, or, in some cases, applied intentionally as manure. A further source of the nitrates contained in soil is to be found, according to some writers, in the free nitrogen of the atmosphere; but of any supply from this source, other than the ready-formed nitrates contained in rain, there is at present no substantial proof.

The production of nitric acid, both from ammonia, and from the organic matter of arable soil, is well illustrated by the field experiments at Rothamsted. The winter drainage-water from the various plots in the experimental wheatfield, is found to contain nitrates nearly in proportion to the quantity of ammonium-salts applied the preceding autumn (*Jour. Roy. Agri. Soc.*, 1873, 334, 337).* While the drainage-water, rich in nitrates, which is obtained at the drain-gauges from soil which has been unmanured for the last eight years, clearly derives the greater part of its nitrogen from the organic matter of the soil.

Many investigations have been made as to the mode in which nitrification takes place. A mixture of nitrogen and oxygen is known to yield nitrous acid when subjected to repeated electrical discharge, but

* For further details see *Jour. Chem. Soc.*, 1871, 286; also *Sixth Report of the Rivers' Pollution Commission*, 58—68; and a lecture by Dr. Gilbert, at the Science Conference at South Kensington, "On Some Points in connection with Vegetation," page 39.

ozone has been shown to be incapable of oxidising gaseous nitrogen. Ammonia may be converted into nitrous and nitric acid either by electric discharges in the presence of oxygen, or by the action of ozone (L. Carius, *Ann. Chem. Pharm.*, clxxiv, 31); but not by ordinary oxygen. Ammonia may also be oxidised into nitric acid, according to some observers (Pesci, Thenard, Knop), by prolonged contact with ferric oxide at ordinary temperatures. With regard to the production of nitric acid from nitrogenous organic bodies, very little seems to be known. It is generally assumed that when such bodies decay in a porous medium, offering a sufficiently large surface for oxidation, nitrates must necessarily be formed, especially if a salifiable base be present; but this view, as far as I am aware, has never been confirmed by exact experiments. The action of ordinary oxygen upon organic matter is supplemented, in the theory of some writers, by the action of ferric oxide and of ozone.

In February of the present year Schlœsing and Müntz laid before the French Academy (*Compt. rend.*, lxxxiv, 301) the results of an experiment, proving, in their opinion, that nitrification was due to the action of an organised ferment; that, in fact, it was probably a function of some low form of vegetable life. This theory of nitrification they further state was regarded as probable by Pasteur as far back as 1862. Pasteur, in view of the active oxidation induced by mycoderms in various kinds of organic matter, expressed the opinion that nitrification required to be studied over again from this point of view. As the experiment of Schlœsing and Müntz formed the starting point of the trials at Rothamsted, it will be necessary to give a brief account of their research.

The primary object of these experimenters was to ascertain if the presence of humic matter was essential to the purification of sewage by soil. To this end they took a glass tube one metre in length, and filled it with a mixture of ignited quartz sand and powdered lime-stone; 5 kilos. of sand, and 100 grams of lime-stone were employed. The column of purely mineral soil thus prepared was supplied with sewage at such a rate that the sewage took eight days to pass through the soil.

During the first 20 days the sewage passed through unaltered; but after that time nitric acid began to appear in the filtrate, and rapidly increased till the filtered sewage contained no longer any ammonia, but nitrates only. The authors ask—If it was a simple case of oxidation, why did 20 days elapse before the commencement of the reaction? If, on the other hand, the seeding and growth of germs was necessary before the soil could become effective, the reason of the delay in nitrification is at once apparent.

After passing sewage four months with complete oxidation of its

ammonia, the authors placed a small vessel of chloroform at the top of the column, and allowed the vapour of the chloroform to pour continuously upon the soil. Müntz had shown in an earlier investigation (*Compt. rend.*, lxxx, 1250), that chloroform effectually suspends the action of organised ferments, while it has little or no action upon soluble ferments. In 10 days after the introduction of chloroform vapour all nitrates had disappeared in the exit water, and the sewage passed through the soil quite unchanged; nitrification had thus plainly been effected by some agent, the activity of which was destroyed by the presence of chloroform.

After supplying chloroform for 15 days, the vessel containing it was withdrawn. Nitrification did not resume with the removal of the chloroform. After about seven weeks, during which the sewage passed unchanged, the attempt was made to seed the column of sand afresh with the organisms necessary for nitrification. For this purpose 10 grams of a vegetable soil, known to nitrify with ease, were washed with water, and the turbid washings poured upon the column of sand. Eight days after this application nitrates again appeared in the exit water. As the sewage took eight days to traverse the column of sand, this was the shortest time in which nitrification could become apparent.

Such is the investigation of Schlœsing and Müntz. They conclude that in the instance before them, and in other cases of rapid nitrification, oxidation is produced through the action of a living organism; but they are careful not to assert that this is the only mode in which nitrification can take place.

The importance of this new theory of nitrification is clearly very great. As the amount of nitrates occurring in soils of known history is at present being investigated at Rothamsted, it was thought advisable to submit the new theory without delay to the test of further experiment. The conclusion of Schlœsing and Müntz is clearly based on two distinct lines of proof. Firstly, the action of antiseptic vapours in preventing nitrification. Secondly, the possibility of inducing nitrification by seeding with a substance already nitrifying. We will describe, in the first place, the experiments made under the former head of inquiry.

A soil was taken from the surface of a kitchen garden, the collection being made after heavy rain, when there was, consequently, but little nitrate present. The soil was air-dried, crushed, and sifted, and the fine soil employed for the experiments. Two series of experiments were made with this soil, but as the general method was in each case the same, one description of the plan followed will suffice.

Four glass tubes were taken, in each of which 100 grams of soil were placed. In the first experiment these tubes were of unequal

length; in the second trial the tubes were all 12 inches in height. In the first experiment the tubes were filled with the dry soil, and 10 c.c. of water gradually added afterwards; the result was that only the upper half of the column of soil became visibly wet. In the second experiment the soil was uniformly mixed with 20 c.c. of water before its introduction to the tubes, the whole of the column was thus in a moist condition. The lower end of each of the four tubes was connected with a small water-pump, which served as an aspirator, while the upper end was connected with a U-tube containing pumice drenched with very dilute sulphuric acid. This U-tube ensured the supply of moist air to the soil, and cut off any ammoniacal vapours that might be present in the laboratory. In the case of three out of the four soil tubes a 10 oz. bottle, containing a few pieces of sponge, and provided with a cork and two tubes, was interposed between the soil tube and that containing pumice and sulphuric acid. The sponge in one of these bottles was moistened with a small quantity of liquid carbolic acid. The sponge of a second bottle received bisulphide of carbon. The third bottle received chloroform. The carbolic acid being little volatile, was not renewed during the course of an experiment. Of the bisulphide of carbon and chloroform 5 c.c. were used on the first day of the experiment, and on every seventh day a fresh quantity of 2 c.c. was placed on the sponge. As these liquids are very volatile, it is evident that during a great part of both experiments the amount of bisulphide of carbon and of chloroform carried to the soil must have been extremely small. The result of the whole arrangement was that through one soil tube moist air free from ammonia could be aspirated; and that in the case of the remaining three tubes the moist air reached the soil more or less charged with antiseptic vapours. Aspiration was carried on for 1 to 1½ hour, through each tube, nearly every day.

The first series of experiments commenced on June 29th, and concluded on August 7th, lasting in all 39 days. The second series commenced on September 24th, and lasted till November 9th, or 46 days.

At the conclusion of both experiments the soil in each tube was extracted with hot water, the chlorine removed with sulphate of silver, and the nitric and nitrous acid present finally measured as nitric oxide gas after the method of Crum and Frankland.* A considerable amount of froth was in most cases produced in the shaking tube, and in some instances the whole of the gas could not be removed from the shaking tube to the eudiometer; the determinations which are too

* The above is but an outline of the process used; the exact mode of treatment found most suitable in determinations of nitrates in soil will probably be described on a future occasion.

low from this cause are marked in the following table with an asterisk. The determinations belonging to the second series of experiments were, as the result of more experience, more accurately done than those in the first series. A summary of the results will be found in the following table:—

Nitrogen as Nitrates and Nitrites per Million of air-dried Soil.

History of Soil.	First Experiment.	Second Experiment.
Original soil.....	6·12*	8·91
Air passed	46·87	50·86
„ with carbolic acid	17·20	40·77
„ „ carbon bisulphide ..	6·70*	9·75
„ „ chloroform	9·48	7·86*

It is evident at once on a review of these figures, that a very large amount of nitrification was determined in each case by aspirating ordinary air through the garden soil, the amount being greatest in the second experiment, in which the soil contained more water, and was equally moistened throughout.

The effect of carbolic acid vapour in preventing nitrification is in both cases imperfect, though much less so in the first experiment than in the second. The fact admits, I believe, of explanation. Carbolic acid enters but slowly into vapour at ordinary temperatures, the vapour is also soluble in water. In the second series of experiments the temperature of the laboratory was lower, the tube containing the soil was longer, and the soil uniformly wet. A smaller amount of carbolic vapour would thus enter the soil than in the first experiment, and the quantity so entering would be retained in the upper portion of the moist soil, while nitrification went on unhindered below. In fact, when the tube was taken down at the end of the experiment, it was found that the cotton wool placed at the lower end of the tube was covered with mould, and no smell of carbolic acid could be perceived; while the wool at the upper end of the tube was quite clean, and the odour of carbolic acid manifest. In the first experiment, as already mentioned, only the upper half of the column of soil was really wet; here nitrification was checked by the carbolic acid, while below nitrification could proceed but slowly from lack of moisture. We learn from this experiment, that carbolic vapour cannot be successfully employed as an antiseptic when any penetration of a moist porous body is demanded, whereas bisulphide of carbon fulfils such requirements excellently. In the case of the soils treated with chloroform and bisulphide of carbon, the cotton wool was found perfectly clean at both ends of the column, and the odour of the vapour was perceivable at the bottom as well as at the top. The quantity of nitrate found in these soils is so little different from that present in the soil before aspiration, that we may

safely conclude that in these two cases no nitrate, or at least an insignificant amount, has been produced in the course of the experiment.

The result of this branch of the investigation is, therefore, to prove that chloroform vapour will effectually prevent nitrification in a soil rich in vegetable matter, a fact directly confirmatory of Schlœsing and Müntz's result obtained with sewage. We also learn that bisulphide of carbon is equally effective with chloroform, and that carbolic acid is probably effective to the extent in which it comes in contact with the soil. It thus appears that antiseptics, as a class, are inimical to nitrification; a result which is hard to explain if this process be one of simple oxidation only.

We turn now to the experiments made at Rothamsted upon the second branch of the inquiry. The object aimed at here was to ascertain if nitrification could be induced in a weak solution of chloride of ammonium, by seeding with a small quantity of a nitrifying body.

Four stoppered pint bottles of pale green glass were taken; each was half filled with the dilute solution of chloride of ammonium used in Nesslerising (1 c.c. = ·00005 gram ammonia), to which a small quantity of acid phosphate of potassium was added. The object of the phosphate was to provide food for the organism to be presently introduced. Two of these bottles were placed in the window, and two in a dark cupboard. To one of the bottles in each series was added 1 c.c. of a mixture made by stirring together 1 gram of kitchen garden soil, and 5 c.c. of water. The soil used in this experiment was rich in nitric acid; it had, however, been kept for two or three years in an air-dry condition. The experiment commenced on May 19th.

On June 2nd all the bottles were tested, but no nitric acid found. Thinking that the slight acidity of the solution might be unfavourable to nitrification, a little freshly precipitated carbonate of calcium was at this date added to each bottle.

On July 11th the solutions were again tested, but no nitric acid found. In the bottle seeded with garden soil, and exposed to daylight, a film of green growth had commenced on the bottom of the bottle. Thinking that the solutions might be too strong, or that the germs of the garden soil had lost their vitality by long keeping, the bottles were now in every case filled with water to the shoulder, and the two bottles already seeded received in each case 1 gram of surface soil, obtained three weeks previously from a "fairy ring." It need hardly be stated that the "fairy-rings" found in meadows contain in the circle of luxuriant grass a more or less vigorous growth of fungi. A sample of the soil beneath the ring had in this case been taken to the depth of 12 inches; this sample contained in its upper part a small quantity of mycelium. The whole 12 inches was air-dried, crushed, and sifted, and from the fine soil 1 gram taken for each of the seeded bottles.

The bottles were next examined on October 11th. No nitric acid was found in either of the unseeded bottles. In the seeded bottle standing in daylight the green growth had increased. No nitric acid was found in this bottle; the application of the Nessler test proved that ammonia was still abundant. With the seeded bottle preserved in darkness the case was wholly different; here abundance of nitric acid was found,* amounting to 18·89 parts of nitrogen per million, while the Nessler test showed that ammonia had completely disappeared. The exact strength of the chloride of ammonium solution before nitrification was unfortunately not known, as at the previous examination it had been diluted with about its own volume of water. If the dilution had been exactly to twice its volume, it would have contained 20·58 parts of nitrogen per million.

We have here, then, a complete nitrification of an ammonium salt, brought about without any attempt to aërate the fluid, by the simple addition of a little soil from a fairy-ring, and of small quantities of phosphates, potash, and lime. The action also takes place exclusively in the dark, the perfectly similar mixture exposed to daylight exhibiting no nitrification.

It was evident that if the solution just obtained was really full of nitrifying organisms, it ought to be capable of acting itself as seed, and of setting up nitrification in other solutions. On October 15th th bottle containing the completely nitrified solution was shaken, an 1 c.c. of the contents added to each of the bottles—one in daylight, and the other in darkness—which had as yet remained unseeded.

On November 6th the solutions were examined. That in the window showed no nitric acid; that in the cupboard contained a trace, amounting to about 0·72 parts of nitrogen per million. Thinking that the nitrifying organism might require organic carbon for its growth, which these solutions did not supply, 50 milligrams of acid tartrate of potassium were added to each bottle.

On November 19th the solutions were again examined. That in daylight still showed no nitric acid. That in darkness now contained nitric acid equal to 2·04 of nitrogen per million.

On December 3rd the nitric acid in the solution kept in darkness had risen to 11·89 of nitrogen per million; but in the corresponding bottle in the window none was found. The experiment is still in progress.†

* The examination for nitric acid, and its quantitative determination, was made by means of indigo (*Chem. News*, xxxv, 45, 57). This method is admirably suited for such a purpose. 10 c.c. of the solution were sufficient for qualitative testing, and a few successive experiments with 10 c.c. sufficed for a quantitative determination.

† On December 19th the nitric acid had increased to 20·06 parts of nitrogen per million; a trace only of ammonia was present. The bottle in daylight still contained no nitric acid.

We have here, then, fresh proof that nitrification can be started in one solution from another, when without such seeding no nitrification would take place. The conclusions of Schlœsing and Müntz are thus again confirmed, with the addition of the important fact that darkness is apparently essential to the action of the nitrifying germs.

That the nitrification observed in soils and waters is due to the growth of some mycoderm, must now be considered as highly probable. The process thus becomes perfectly analogous to the acetic fermentation, in which alcohol is oxidised by the growth of *Mycoderma aceti*. The mycoderm producing nitrification has probably special characters, and might be sought for by a microscopical examination of the nitrified solutions already described. This part of the investigation must, however, be left to other observers.

Postscript.—January 4th, 1878.—In a paper read before the Royal Society, on December 6th, it is shown by Messrs. A. Downes and T. P. Blunt, that light is inimical to the development of bacteria, a few hours' exposure to daylight being in many cases sufficient to destroy all the germs existing in an organic fluid, while similar solutions kept in darkness developed bacteria freely. The bearing of this observation on the fact already recorded as to the influence of light on nitrification is obvious. The influence of light on nitrification was not apparently quite unknown; it is twice hinted at in Gmelin's Chemistry (*Cavendish Society's Translation*, iii, 68; vii, 92), but is not mentioned by most writers on the subject.

V.—*The Gas of the Grotta del Cane.*

By T. Graham Young.

Some time ago my attention was drawn to the abstract of a paper which appeared in the *Chemical News* (vol. xxxv, page 21), giving the results of some analyses of the gas from the Grotta del Cane, near Naples, by E. A. Finot.

The results of these analyses tend to show that the residual mixture of nitrogen and oxygen, after absorption of the carbonic acid, contains a larger proportion of oxygen than common air. Being desirous of accounting for the excess of oxygen, I took the opportunity of being in the neighbourhood of the grotto to procure samples of the gas in sealed tubes. The temperature of the air in the cave above the layer of gas is very different from that of the gas itself, as the following table shows:—

	April 12, 1877.	April 27, 1877.	April 28, 1877.
Temperature outside cave in shade.....	17°	20°	20°
Temperature about 2 yards inside the cave, and 2 feet above layer of gas.....	21°	21°	25°
About 2 inches above layer of gas.....	25·5°	—	—
About 2 inches below layer of gas	32°	—	—
On floor of cave	36°	38°	39°
About 2 yards still further into cave on floor..	40°	40°	40°

The gaseous layer is completely saturated with aqueous vapour. The floor of the cave inclines downwards, and likewise the roof, so that, after proceeding about five yards, the gas is level with the roof, which prevents further ingress.

On carrying a lighted torch into the cave, its smoke gradually falls, till it reaches the layer of gas, upon which it settles; and on looking in, the surface of the gaseous layer is seen, resembling that of water, and appears covered with beautiful undulations.

On holding the head below the level of the gas, holding the breath, and keeping the eyes open, an intolerable prickling sensation is produced upon the eyes by the carbonic acid.

A dog brought into the cave, as is the custom there, appears, as it were, to drink the gas, lapping with its tongue. Then its eyes begin to dilate to an unnatural size, and its lapping becomes more spasmodic; beyond this it does not seem to suffer. While in the cave, also, the dog was able to stand, but when carried and set on its feet outside in the fresh air, it fell, and lay struggling as if in paroxysms of suffocation, but recovered in two or three minutes. I was told, however, that the animal gets into such a nervous state with the prospects of its frequent ordeals, that it has to be killed in three months.

On analysing the gas, I get results contrary to those obtained by M. Finot, as regards the excess of oxygen.

I find no excess of oxygen, but an amount nearly corresponding with that contained in common air; also a much larger proportion of carbonic acid than that found by M. Finot.

The carbonic acid varies from 61·5 to 71 per cent. The following is a comparison of the results:—

	According to Young.				According to Finot.			
CO_2	61·50	71·00	Residual air		25·38	25·69	Residual air	
O	7·80	5·80	20·25	20·00	18·46	20·13	24·74	27·10
N	30·70	23·20	79·75	80·00	56·16	54·18	75·26	72·90
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

VI.—*On some Derivatives of Allylacetone.*

By J. K. Crow, B.Sc., Dalton Scholar in the Chemical Laboratory of Owens College.

University of Michigan

Allylacetone, $CH_3—CO—CH_2(C_3H_5)$, or $\begin{cases} CH_2(C_3H_5) \\ | \\ CO \\ | \\ CH_3 \end{cases}$, was first prepared by Zeidler, who obtained it by decomposing allylacetoacetic ether with potash, in the usual manner in which all acetoacetic ethers are decomposed. As this ketone contains a double linking, it appeared interesting to try the action of nascent hydrogen upon it, for the purpose of determining whether the addition of hydrogen takes place in the position of the double linking in the chain, or whether this reaction is the same as in other cases, an alcohol being formed.

The acetone was prepared according to Zeidler's method, and diluted with its own volume of ether, and the whole transferred to a flask surrounded by cold water, and containing also a quantity of water about twice as large in volume as that of the ethereal solution of the acetone. The flask was connected with a reversed condenser, and sodium cut in thin slices dropped gradually in, until about half as much more of the metal had dissolved as was theoretically needed for the reaction. The ethereal solution was then separated by a funnel from the watery part, and dried with potassium carbonate. After the ether was distilled off, the greater part of the remaining liquid came over from 135° to 140°. This portion, after repeated fractional distillations, yielded the pure substance boiling at 138—139°. It was dried over anhydrous copper sulphate, and analysed with the following results:—

(*a*.) 0·1064 gram substance yielded on combustion 0·2795 gram CO_2, and 0·1148 gram H_2O.

(*b*.) 0·1152 gram substance gave 0·3025 gram CO_2 and 0·1255 gram H_2O. These numbers point to the conclusion that the liquid has the formula $C_6H_{12}O$.

	Calculated for this formula.	Found. *a*.	Found. *b*.
C	72·00	71·64	71·61
H	12·00	11·99	12·10
O	16·00	—	—
	100·00		

The liquid appears to be an alcohol of the allyl series, as if possesses

the power of combining very violently with bromine, and yields an acetate when heated with acetic anhydride. It has a sweet, but at the same time rather pungent odour, somewhat resembling that of allyl alcohol. It is soluble to a slight extent only in water, but freely in alcohol and ether. It appears to be a secondary alcohol, and a homologue of allyl alcohol, and has the graphic formula—

$$CH_3—CHOH—CH_2—CH_2—CH=CH_2.$$

The specific gravity of the alcohol was found to be 0·842 at 16·2°, compared with water at 17·5°.

Its acetate was obtained by gently heating the alcohol in a flask connected with a reversed condenser, with acetic anhydride in excess. The product was then washed with a dilute solution of potassium carbonate, dried, and distilled; the acetate was obtained, boiling between 147—149°, as a colourless liquid of a pleasant refreshing odour. It was analysed, with the following results:—

(*a.*) 0·1991 gram of the substance gave 0·491 gram CO_2 and 0·1766 gram H_2O.

(*b.*) 0·1570 gram of substance gave 0·3877 gram CO_2 and 0·1397 gram H_2O.

	Calculated for the formula $C_6H_{11}OC_2H_3O$.	Found. *a.*	*b.*
C	67·61	67·26	67·35
H	9·86	9·86	9·88
O	22·53	—	—
	100·00		

As before remarked, the alcohol combines very readily with bromine. In order to obtain the bromine compound, a mixture of the alcohol with chloroform was placed in a flask surrounded by cold water, and connected with a condenser. Bromine was then gradually added from a dropping funnel until it effected a permanent coloration of the liquid; the chloroform was then distilled off under reduced pressure, to prevent the bromo-compound from decomposing; and the resulting product, which was thick and slightly brown, was dried over sulphuric acid and lime. The mass does not crystallise, and cannot be distilled; it has a most pungent odour, its vapour attacking the nostrils. The following analyses show that it has the formula $C_6H_{12}Br_2O$, and is an addition-product of one molecule of bromine to one of alcohol.

0·1604 gram of substance gave 0·2196 gram AgBr and 0·0088 gram Ag.

0·1038 gram of substance gave 0·1487 gram AgBr and 0·0007 gram Ag.

(*a.*) 0·2305 gram of substance yielded on combustion 0·2314 gram CO_2 and 0·0947 gram H_2O.

(*b.*) 0·410 gram of substance gave 0·4105 gram CO_2 and 0·1685 gram H_2O.

	Calculated from formula $C_6H_{11}Br_2OH$.	Found. *a.*	*b.*
C	27·69	27·38	27·31
H	4·61	4·56	4·57
Br	61·54	61·97	61·45
O	6·16	—	—
	100·00		

This dibromide was heated with silver acetate in sealed tubes, to obtain a diacetin, but without success, as the body decomposed too rapidly on heating. An attempt to substitute hydroxyl for bromine by heating the substance in sealed tubes with water also failed.

When this body is boiled with K_2CO_3 solution, a clear oily liquid distils over with the steam; it has a smell very similar to that of the dibromide, but contains an atom of bromine less. On analysis 0·2804 gram of substance gave 0·1484 gram AgBr and 0·0064 gram Ag, which corresponds with 41·03 per cent. of bromine, the percentage required by the empirical formula $C_6H_{11}Br(OH)_2$ being 40·40.

VII.—*Note on Tetrabromide of Tin.*

By Thomas Carnelley, D.Sc., Assistant Lecturer on Chemistry in The Owens College, and L. T. O'Shea.

It having been necessary to prepare a quantity of tetrabromide of tin for a research on the melting points of metallic salts, in which one of us is engaged, it is thought that a short account of this body will not be without interest, especially as, with two exceptions, there has not been published any previous account concerning it. One of these occurs in Balard's well-known research on bromine (*Ann. Chim. Phys.*, xxxii, 337). His account of it, however, is very incomplete, neither melting point, boiling point, nor analytical numbers, &c., being given, for he merely says that by heating tin in bromine a white crystalline substance is obtained, which is easily fusible and volatile. The

second reference is that of Bœdeker, in his *Beziehungen Zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen* (Leipsig, 1860), where he simply gives the specific gravity and melting point.

In order to prepare stannic bromide, a piece of combustion-tubing was bent thus,

, and a quantity of metallic tin placed in the bend *c*, and heated to the melting point by a lamp; bromine was then gradually dropped into the bend *b*, by means of a tap-funnel attached to *a*. On the bromine passing over the tin, the latter burnt with a very faint violet flame, while the tin bromide formed condensed in the bend *d*. The burning of the metal can be kept up continually by properly regulating the flow of bromine, and would serve as a very good lecture experiment. The distillate obtained was freed from excess of bromine by redistilling repeatedly, till the liquid which passed over was quite colourless. On slightly cooling, or even without, it solidified to a mass of beautiful colourless crystals of pure stannic bromide.

Tetrabromide of tin melts at 30° C., and boils without decomposition at 201° (uncorrected); a large quantity distilled entirely at this temperature, without the thermometer showing the slightest alteration. On exposure to the air at the ordinary temperature it does not fume, and is only very slowly decomposed, but on gently warming it gives off white vapours of oxide of tin. It dissolves in cold water without decomposition, but after standing several hours it is gradually decomposed, hydrate of tin being precipitated; boiling, however, hastens the decomposition, as does also the addition of nitric acid, which in the hot solution precipitates the whole of the tin almost immediately, with a slight evolution of bromine. The specific gravity, according to Bœdeker (*vide supra*) of a specimen of tin tetrabromide melting at 39° was 3·322.

Analysis.—The tin was determined by evaporating to dryness with nitric acid, igniting, and weighing the oxide of tin produced. For the estimation of the bromine a weighed portion was boiled with dilute nitric acid in a flask provided with a tube dipping under ammonia, so as to retain any hydrobromic acid that might be given off. On cooling, the hydrate of tin was filtered off, and the filtrate, to which the ammoniacal solution had been added, mixed with sulphurous acid to reduce any free bromine, and the bromine determined in the ordinary way with silver nitrate.

(1.) ·9244 gram of substance gave ·3188 gram SnO_2 = 27·13 per cent. of Sn.

(2.) ·7572 gram of substance gave ·2610 gram SnO_2 = 27·11 per cent. Sn.

(3.) ·9523 gram of substance gave 1·6210 gram AgBr and ·0044 gram Ag = 72·78 per cent. Br.

		Calculated.	Found. (1)	(2)	(3)	Mean.
Sn	=	26·94	27·13	27·11	—	27·12
Br	=	73·06	—	—	72·78	72·78
		100·00				99·90

Determination of Vapour Density.—As the compound distilled without the least sign of decomposition, its vapour density was determined by Dumas' method, with the following results:—

		I.	II.
Weight of bulb + air	=	2·4697	4·985
Temperature of air.....	=	16° C.	13° C.
,, oil bath....	=	228°	260°
Weight of bulb + vapour .	=	2·6415	5·157
Capacity of bulb.....	=	17·1 c.c.	19·5
Barometer	=	741	731

The small bubble of air was measured and allowed for in the second experiment, but not in the first.

		Found. (1)	(2)	Mean.	Calculated for $SnBr_4$.
Vapour density..	=	230·6	227	229	219

VIII.—*On Potable Waters.*

By Edmund J. Mills, D.Sc., F.R.S., "Young" Professor of Technical Chemistry in Anderson's College, Glasgow.

A completely satisfactory method of examining potable waters involves the solution of a considerable number of important chemical problems, and must long continue to require the thought and labour of many experimenters. These problems have occupied much of my attention during the last two years, in consequence of my undertaking to report every month on the quality of the water which is derived from Loch Katrine and supplied to Glasgow.

With respect to the organic constituents of waters two principal processes have been proposed. In the first of these (Wanklyn, Chapman, and Smith, *Chem. Soc. J.*, xx, 445) the unconcentrated mixture

of organic impurities (for a mixture we must assume it to be) is boiled with alkaline permanganate, and the ammonia thereby evolved is regarded as a measure of the impurity present. This process is simple and elegant, and will probably form a leading feature in our future methods, for it admits of graduation, and may serve to distinguish one impurity from another. Unfortunately, however, it deals with bodies at present unknown, in a manner of which we are ignorant; its results therefore admit of no precise interpretation, and (as has been justly remarked) (*Sutton's Volumetric Analysis*, 3rd edit., p. 345) can aid only to distinguish a bad water from a good one. According to the second process (*Chem. Soc. J.*, xxi, 77) the water is concentrated, usually after the addition of a reducing agent, and the residue submitted to combustion in a vacuum with cupric oxide in presence of copper. Now substantially satisfactory evidence has been adduced that there is no material loss during the evaporation. It is easy therefore, by a suitable mode of collecting and analysing the gases of combustion, to determine exactly the total amounts of carbon and nitrogen extractable from the organic mixture present in the water. This process admits of no graduation, and can never distinguish between one organic impurity and another associated therewith. Happily, however, it furnishes two familiar fundamental data in a manner well understood by chemists, and its results are precisely interpretable. Hence it forms the philosophical starting-point in an endeavour to solve the problems of water-analysis. It will be referred to exclusively in the following pages.

I. Errors and Blanks.

Probable Error of the Results.—In their first paper on this subject (*loc. cit.*, pp. 93, 94), Frankland and Armstrong gave various determinations of organic carbon and nitrogen in small quantities of sugar, urea, and hydric hippurate, &c. Assuming 100 as the weight of organic carbon or nitrogen taken, I find their analyses lead to the following figures:—

Substance.	No. of determinations.	Prob. error per cent. of one determination.
Organic carbon	10	5·96
,, nitrogen.....	6	7·35

I entertain little doubt, from my own experience, that this uncertainty must have rapidly diminished, though it would naturally enough occur in the case of anyone inventing this process and then using it for the first time. In 1874 (Sixth Report of the Rivers' Commission, p. 505), Frankland obtained further results with some quinine solutions. Three of these deal with too minute quantities to

be fairly taken into account for probable error; the remaining five furnish the following results:—

Substance.	No. of determinations.	Prob. error per cent. of one determination.
Organic carbon	5	2·84
„ nitrogen.....	5	2·56

These carbon determinations are all rather too high, the nitrogen determinations all rather too low: they are evidently affected by constant error, for which I cannot give any account. Hence the probable errors in the quinine experiments are greater than those of the process itself. Judging of the results simply by their own mean, the probable error per cent. per single determination reduces to 1·36 for the carbon and 1·44 for the nitrogen. An intermediate number, say 2 per cent., would probably be a very fair estimate.

In order to appreciate the significance of this result, it will be necessary to compare it with others, derived from common analytical figures. Gmelin gives three analyses of cane-sugar (Watts's translation, xv, 247), four of urea (*ibid.*, vii, 365), and five of hydric hippurate (*ibid.*, xii, 72). Considering the theoretical amount of carbon or nitrogen in each case as 100, we arrive at the following conclusion:—

Substance.	No. of determinations.	Prob. error per cent. of one determination.
Organic carbon	12	1·21 } mean 1·96
„ nitrogen.....	8	2·72 }

The carbon determinations are all too low; the nitrogen determinations are apparently free from constant error.

Gmelin also gives (*ibid.*, xvii, 269) five analyses of quinine, of which only the carbon determinations are available for calculating probable error; the necessary data for the sulphate are also lacking. The probable error per cent. of single determination is, in this case, 0·55.

According, then, to Frankland's quinine experiments, the combustion method of water analysis may be taken as now giving a probable error of about 2 per cent. per determination; and our knowledge of the amount of carbon and nitrogen extractable from cannose and urea with hydric hippurate is, as a *whole*, no more accurate than this, according to the analyses cited by Gmelin. On the other hand, the analyses of quinine given by Gmelin are more than thirteen times as valuable as those which Frankland adduces. This disparity, however, is considerably diminished by the fact that quinine is easily brought into a condition for exact weighing, but that its sulphate is not. From several hundred analyses made in my laboratory, in con-

nection with which systematic computations of the above character have been made, it appears that, taking gravimetric and volumetric methods together, the probable error per cent. of a single determination slightly exceeds, as a rule, ·1 per cent. Large numbers of determinations, however, brought forward by Gmelin as evidence of the composition of various bodies, have a considerably greater probable error than even 2 per cent. It appears, then, that the accuracy of Frankland and Armstrong's method compares favourably with that of the ordinary combustion process, and may be safely used as a basis of inference.

Blank Experiments.—The water is, as a rule, evaporated with a constant quantity of hydrosodic sulphite dissolved in a large excess of aqueous hydric sulphite, a trace of ferric salt having been first added if necessary. It is convenient to have the two sulphurous solutions then mixed together. These lead to a constant excess a in the carbon and nitrogen, which excess can be determined by a special combustion of their residue. We may term a the chemical error in the blank. When n cubic centimeters of purified water are evaporated with the sulphites, in order to imitate as closely as possible the proceeding of an analysis, a further excess of carbon and nitrogen is introduced. This is evidently proportional to the number of cubic centimeters of water present, and may be termed the "volume error v." Hence the general form of correction for a blank experiment is $a + nv$, v being the amount of error introduced per cubic centimeter of water.

In order to obtain purified water, it is convenient to heat distilled water to near boiling for about twenty-four hours with alkaline permanganate, and then, after excessive acidification with hydric sulphate, to heat it again for an equal time; in this way the organic matter has a double solicitation to decompose. The acid liquid is finally distilled. A litre of water thus purified from the Loch Katrine supply adds nothing to the chemical error during an evaporation lasting twenty-four hours. It seems probable that the volume error is in most cases very small. I have found the following errors in blank experiments:—

(1) ·000048 carbon, ·000111 nitrogen (a).
(2) ·000047 carbon, ·000114 nitrogen ($a + nv$).
(3) ·000090 carbon, ·000085 nitrogen (a : new chemicals).

Influence of Size of Evaporating Dish.—In the original method, as still carried out by its inventors, the water was evaporated in a round glass dish, having a diameter at the orifice of 4 inches (10·2 centims.). It was proposed by Bischof (*Proc. Phil. Soc. Glasgow*, ix, 21) to increase the diameter of the dish to 6 inches (15 centims.), in order to accelerate the rate of evaporation. The dishes employed in my labo-

ratory have the minimum available diameter, namely, 3 inches (7·6 centims.). In the following table their performance* is contrasted with that of a 6-inch dish, operating at the same time, in the same apartment, and on the same waters:—

		Org. carbon.	Org. nitrogen.
A	3 inch dish	·227	·015
	6 „ „	·203	·027
B	3 „ „	·235	·020
	6 „ „	·214	·018
C	3 „ „	·444	·039
	6 „ „	·438	·041
D	3 „ „	·387	·022
	6 „ „	·375	·050
Means	3 „ „	·323	·024
	6 „ „	·307	·034
	Differences	− ·016	+ ·010

It appears, then, that there is a loss of carbon and a gain of nitrogen by using a 6-inch dish. Owing to the irregular manner in which the organic impurity of the residue is protected by the drying sulphite, the effect also is naturally irregular. A special experiment was made with two pairs of residues in order to ascertain the source of the increase of nitrogen. The residues were added to water, free from ammonia, and distilled with sodic carbonate, as in ordinary ammonia determinations. The results were—

		Ammonia.	
I.	3 inch dish	·025	Diff. ·012
	6 „ „	·037	
II.	3 „ „	·020	Diff. ·010
	6 „ „	·030	

The greater part of the ammonia here found was produced from the peaty matter present in the water by the action of the sulphites with which it was evaporated. The difference between the two results must represent ammonia absorbed from the atmosphere. Its mean amount is ·011, corresponding to ·009 "organic nitrogen," a number very nearly identical with the mean excess (·010) actually found above. It is evident, then, that the use of a 6-inch dish leads to uncertain and inaccurate results. The areas of a 3, 4, and 6-inch dish are to one another as the numbers 1, 1·8, and 4; and the error probably increases rapidly with the area. The problem in fact is, how to evaporate a water in the narrowest possible dish in the shortest possible time.

* I am indebted to Mr. Macnab for the careful carrying out of these experiments.

II. Apparatus.

Evaporator.—The evaporator I employ is represented in the accompanying figure at about one-fourth its natural size. It is constructed of copper, and consists of a cylindrical water-bath, *a*, surmounted by a hemispherical cover, *b*, which stands in a water-joint. In the platform of the bath is placed a 3-inch glass dish, *c*; this is held down steam tight against an india-rubber band by the three clamps *d*.

Evaporator. (Scale ¼.)

There is an aperature, *e*, in the cover, through which and a simple stuffing arrangement enters the constant feed of water to be analysed. The cover is kept cool by a continuous supply of cold water through a number of jets in the circular pipe, *f*. This water becomes warm by the time it has flowed down to the water-joint; which, in its turn, delivers it to a discharge pipe, *g*, and thence to the constant feed, *h*, for the water-bath. The remaining orifices of the bath are three. Of these, *k* is the steam exit; *l* is the entry, *m* is the exit for a current of aspirated air. This air, having been first passed over purified pumice moistened with somewhat dilute hydric sulphate, traverses two coils at the base of the interior of the bath; thus heated, it ascends a chimney whose summit is a little above the rim of the dish on the right hand side of the figure. It then strikes to the left across the dish; and descending a similar pipe whose orifice is level with the dish's rim, passes through *m* to an aspirator, which is fixed to the tap. The air is thus unfavourably disposed for giving up anything absorbable by the evaporating liquid; and, in fact, has no chemical influence on the process. The cooled cover condenses 6 cub. centims. an hour. With a current of air amounting to 360 litres an hour, the total evaporation is rather more than 45 cub. centims. an hour; with a current of 1062 litres, the total evaporation would be 100 cub. centims. an hour.

Convectionless Feed.—In Bischof's apparatus (*loc. cit.*, p. 22), the supply passes from the reservoir to the evaporating dish through a straight tube. There is, consequently, convection through this tube to the reservoir; and that is necessarily attended with much loss of heat. It is, moreover, objectionable to heat the delicate organic matter of waters (and especially of peaty waters) any longer than is strictly necessary. I have therefore contrived a convectionless feed. Its principle is very simple. The delivery tube, instead of being straight, is bent in two places; the consequence of which is that, at the end of each regurgitation, two long bubbles of air, *nn*, always remain entrapped. Between these and the tube, the layer of water is so thin, that convection to their left becomes impossible. The heat that would otherwise escape is thus locked up within the evaporator, and the water to be analysed is not heated until the last moment. So effectually is convection arrested, that, with the first made (and rather imperfect) feed of this kind, and a rate of evaporation considerably exceeding 100 cub. centims. an hour, it took four hours for some rather strong hydrochloric acid in the dish to redden blue litmus in the reservoir.

The evaporator also works as a whole so steadily that, if a scale be applied to a reservoir of suitable shape, the diurnal changes of the barometer can be accurately integrated by its means.

University of Michigan

III. Natural Constants.

Living plants and animals consist of a large number of compounds which undergo transformation after death; and it is an accepted belief, for which much evidence can be adduced, that in such transformation those compounds are greatly reduced both in number and complexity. The natural oxidising action whereby this end is attained is known to be very efficient when conducted in the soil, and more particularly through great depths of soil. Hence we may expect that in water gathered considerably below the earth's surface, or in some equivalent situation, there will be very few organic compounds, or even one alone; in short, that we shall be dealing with a case of what Chapman designated "limited oxidation." The ratio of organic carbon to organic nitrogen must, under this condition, approximate to one or more of the ordinary chemical ratios, $C_n : C_m$: and; if constant, it may be termed a "natural constant in potable waters."

The Sixth Report of the Rivers' Commission (London, 1874), contains an enormous number of analyses of waters taken from every variety of geological formation, and must ever remain one of the principal monuments of scientific industry in connection with natural waters. I have carefully examined the whole of that Report. The result is, that the great majority of the returns show no satisfactory evidence of chemical constants:—the polluted or turbid waters for an obvious reason; the clay effluents, because oxidation in clay is too languid; springs from certain coal measures, because they are in fact polluted by coal, &c.; in some cases, the figures are promising but too few. There are, however, three groups of data that do lead up to the object of which I was in quest, as might indeed have been expected of them; these refer to unpolluted ("clear" or "slightly turbid") waters from deep wells, and from land unmanured and uncropped,—to which may be added the results of an investigation into the effect of filtration through spongy iron.

(α) I. *Deep Wells in the Chalk.* (Report, pp. 99—101.)—The following table contains the organic analyses of fifty waters:—

TABLE I.

No.	Locality.	Organic Carbon.	Organic Nitrogen.	Remarks.
I.	Brighton.	·048	·009	Clear and palatable.
II.	,,	·055	·011	,,
III.	Bury St. Edmunds.	·089	·020	,,
IV.	Canterbury.	·012	·012	,,
V.	Deal.	·032	·013	,,
VI.	,,	·050	·007	,,
VII.	,,	·056	·024	Slightly turbid; palatable.
VIII.	Dorchester.	·040	·010	Clear and palatable.
IX.	Dover.	·034	·008	,,
X.	,,	·028	·005	,,
XI.	Dunbridge.	·044	·005	,,
XII.	Great Grimsby.	·025	·007	,,
XIII.	Hull.	·032	·012	,,
XIV.	,,	·093	·016	,,
XV.	Ipswich.	·064	·017	,,
XVI.	Norwich.	·074	·027	,,
XVII.	Ramsgate.	·052	·013	,,
XVIII.	Sudbury (Suff.).	·050	·012	Slightly turbid; palatable.
XIX.	,,	·045	·007	Clear and palatable.
XX.	Taverham.	·059	·024	,,
XXI.	Thames Basin.	·076	·009	,,
XXII.	,,	·041	·016	,,
XXIII.	,,	·029	·007	,,
XXIV.	,,	·035	·030	Slightly turbid; palatable.
XXV.	,,	·041	·026	Clear and palatable.
XXVI.	,,	·034	·018	,,
XXVII.	,,	·027	·006	,,
XXVIII.	,,	·071	·026	,,
XXIX.	,,	·020	·006	,,
XXX.	,,	·028	·009	,,
XXXI.	,,	·049	·006	,,
XXXII.	,,	·031	·005	,,
XXXIII.	,,	·040	·007	,,
XXXIV.	,,	·048	·005	,,
XXXV.	,,	·044	·007	,,
XXXVI.	,,	·056	·011	,,
XXXVII.	,,	·030	·009	,,
XXXVIII.	,,	·058	·018	,,
XXXIX.	,,	·064	·017	,,
XL.	,,	·019	·012	,,
XLI.	,,	·026	·008	,,
XLII.	,,	·081	·011	,,
XLIII.	,,	·051	·017	Slightly turbid; palatable.
XLIV.	,,	·033	·014	Clear and palatable.
XLV.	,,	·131	·010	,,
XLVI.	,,	·052	·024	,,
XLVII.	,,	·036	·010	,,
XLVIII.	,,	·030	·015	,,
XLIX.	,,	·042	·011	,,
L.	Winchester.	·048	·018	,,

Assuming that all the determinations have the same "weight," the method of least squares (which will be used throughout) leads to a

ratio, $\frac{\text{org. carbon}}{\text{org. nitrogen}} = 3{\cdot}089$, with a probable error of ·26 (or 8·3 per cent.) for the mean. When it is remembered that, in nineteen of the nitrogen determinations, the amount actually obtained is in the third place of decimals of a part per hundred thousand, such a probable error appears exceedingly moderate. If we were to omit determination XLV as exceptional or accidental, we should find $\frac{\text{org. carbon}}{\text{org. nitrogen}} = 2{\cdot}993$, with a probable error of ·23 (or 7·6 per cent.): but, in the absence of direct evidence, this proceeding would be illegitimate.

II. *Effect of Filtration through Spongy Iron.* (Report, p. 220).—There are fourteen experiments, the original water having been the Chelsea supply.

TABLE II.

No.	Locality.	Organic Carbon.	Organic Nitrogen.	Remarks.
I.	Chelsea.	·025	·004	Clear.
II.	„	·046	·015	„
III.	„	·063	·035	„
IV.	„	·070	·047	Turbid.
V.	„	·060	·008	Clear.
VI.	„	·120	·031	„
VII.	„	·097	·023	Slightly turbid.
VIII.	„	·060	·015	Clear.
IX.	„	·113	·027	Contained suspended particles.
X.	„	·077	·021	Slightly turbid.
XI.	„	·048	·009	„
XII.	„	·073	·013	„
XIII.	„	·077	·012	Clear.
XIV.	„	·089	·020	„

Hence we obtain the ratio 3·015, with a probable error of ·40 (or 13·4 per cent.). This quotient is substantially the same as the preceding. "Weighting" the two in accordance with their probable errors, we arrive as a mean result at 3·067, with a probable error of ·22 (or 7·2 per cent.).

(β) I. *Deep Wells in the Devonian, Millstone Grit, and Coal Measures.* (Report, pp. 89—92.)—There are eleven available determinations.

TABLE III.

Unpolluted Deep Wells (Devonian).

No.	Locality.	Organic Carbon.	Organic Nitrogen.	Remarks.
I.	Ivybridge.	·021	·005	Slightly turbid; palatable.
II.	Mansfield.	·053	·014	„
III.	Arbroath.	·046	·011	Clear and palatable.

No.	Locality.	Organic Carbon.	Organic Nitrogen.	Remarks.
	Unpolluted Deep Wells (Millstone Grit).			
IV.	Glossop.	·092	·020	Clear and palatable.
	Unpolluted Deep Wells (Magnesian Limestone).			
V.	Mansfield Woodhouse.	·139	·039	Slightly turbid.
VI.	Pontefract.	·054	·021	Clear.
VII.	Sunderland.	·035	·030	„
	Unpolluted Deep Wells (Coal Measures).			
VIII.	Accrington.	·045	·017	Clear and palatable.
IX.	Bedlington.	·051	·035	„
X.	Blackburn.	·117	·055	„
XI.	Castleford.	·133	·045	Slightly turbid; palatable.

The ratio is 2·534, with a probable error of ·26 (or 10·1 per cent.).

II. *Drainage from Land Unmanured and Uncropped.* (Report, p. 62.)—The land referred to had been manured with guano and superphosphate in 1868. The determinations, of which nine only can be selected, extend from 1872 to 1874.

TABLE IV.

No.	Locality.	Organic Carbon.	Organic Nitrogen.	Remarks.
I.	Rothamstead.	·108	·045	Clear.
II.	„	·147	·049	„
III.	„	·127	·042	„
IV.	„	·114	·045	Slightly turbid.
V.	„	·096	·032	„
VI.	„	·098	·037	„
VII.	„	·174	·075	„
VIII.	„	·117	·054	Clear.
IX.	„	·098	·042	„

The ratio is 2·520, with a probable error of ·08 (or 3·1 per cent.). Combining this with that found in βI, the result is 2·521, with a probable error of ·07 (or 2·9 per cent.).

γ. *Deep Wells in the New Red Sandstone.* (Report, pp. 93—94.)—There are twenty-four available determinations.

TABLE V.

No.	Locality.	Organic Carbon.	Organic Nitrogen.	Remarks.
I.	Birkenhead.	·041	·038	Clear and palatable.
II.	,,	·047	·015	,,
III.	Birmingham.	·052	·016	Slightly turbid ; palatable.
IV.	,,	·034	·006	Clear and palatable.
V.	,,	·031	·007	,,
VI.	,,	·009	·004	,,
VII.	,,	·037	·012	Slightly turbid ; palatable.
VIII.	Kidderminster.	·015	·004	Clear and palatable.
IX.	Liverpool.	·066	·024	,,
X.	,,	·020	·020	Slightly turbid ; palatable.
XI.	,,	·076	·033	Clear and palatable.
XII.	,,	·018	·013	,,
XIII.	Nottingham.	·050	·020	,,
XIV.	,,	·027	·007	,,
XV.	,,	·039	·035	Slightly turbid ; palatable.
XVI.	,,	·017	·013	Clear and palatable.
XVII.	,,	·026	·019	,,
XVIII.	Wallasry.	·030	·008	,,
XIX.	Wolverhampton.	·041	·014	,,
XX.	,,	·068	·010	,,
XXI.	,,	·032	·011	Slightly turbid ; palatable.
XXII.	,,	·064	·023	Clear and palatable.
XXIII.	Worksop.	·026	·006	,,
XXIV.	,,	·048	·007	,,

The ratio is 2·056, with a probable error of ·27 (or 13·2 per cent.).

The following table contains a summary of the whole of the preceding evidence as to the natural constants of waters.

TABLE VI.

No. of observations.	Constant.	Prob. error of constant.	Calculated.	
64	$\alpha = 3{\cdot}067$	·22	$C_{12} \div N_3 = 3{\cdot}429$	Mean 3·000
20	$\beta = 2{\cdot}521$	·07	$C_{12} \div N_4 = 2{\cdot}571$	
24	$\gamma = 2{\cdot}056$	·27	$C_{12} \div N_5 = 2{\cdot}057$	

The value of these results may be appreciated as follows. It has already been shown (p. 59) that, in certain instances of the ordinary combustion process, the probable error of a single determination of organic carbon is 1·21, of organic nitrogen, 2·72, per cent. If we suppose it required to ascertain the ratio between the two quantities, the quotient will be 1·00, with a probable error of 2·98 per cent. The total evidence for the constant 2·571 is thus rather better than a single determination of the ratio of carbon to nitrogen by the combustion process, as above referred to.* When, however, we find this

* The following instance of the state of our knowledge in some cases of quantitative analysis may be adduced at this point. According to the evidence given by Gmelin

constant to be evidently one of a series of three others, its probability and theirs become very considerably increased. Hence, while trusting that many additional analyses may be brought to bear on diminishing the probable error of these constants, I cannot but think that their establishment has been fairly secured.

These results lead to some not unimportant suggestions. Can we find a porous oxidiser, such that it will reduce the whole of the nitrogenous organic matter to a body or bodies having one of the ratios α, β, or γ? If so, there can be little doubt that the alkaline permanganate process would then give as definite and certain a result as it does now with an alkaloïd.*

The ratio of nitrogen to oxygen in the air is, with small variations, a constant quantity. Its action upon living beings has to a great extent been elucidated, and appears to involve a closed cycle of exchanges between animals and plants; but without this cycle is the region of decomposing beings, its action whereon has hitherto continued unexplained. Now, upon this latter subject, the analyses of the organic matter in waters throw considerable light. The principal constituents of animals, the proteins, have an $n(C_6)$ formula; the principal constituents of plants, the celluloïds, have also an $n(C_6)$ formula. By oxidation in presence of water and the porous earth, all these are, to some extent, consumed; but, in the long run, as we have seen, the $n(C_6)$ formula is preserved, in a set of bodies whose number does not necessarily exceed three. These bodies have a constant composition and, in all probability, a practically constant weight; their continued production, moreover, involves a definite rate of organic change. The mass of the oxygen concerned in their formation must, therefore, be definite. We are, as yet, ignorant of the manner in which nitrogen takes part in the natural chemistry of the earth's surface; but the total amount in the air is finite, and if it be the complement or related to the complement of the amount existing organically in potable waters, its mass must also be definite. We can, therefore, conceive an origin for the constancy of the composition of the air; and seeing that the carbon-nitrogen "ratios" in waters are three at least, we can understand how it has chanced that the oxygen-nitrogen ratio in air is not a definite chemical ratio.

A material alteration in the mass of atmospheric oxygen, or of the porous soil, or of the soil's temperature, would involve a vital chemistry based on some other modulus than $n(C_6)$, and a total change in the aspect of terrestrial existence.

(iii, 321) for the percentage of water in so common a substance as potash-alum, the mean result is 2·51 per cent. above theory; the probable error of this mean is 1·80 per cent., and of a single determination, 3·60 per cent. These errors are considerably enhanced if calculated from the theoretical, instead of the mean experimental number. * I have already performed some experiments in this direction.

IX.—*On a Fourth New Method for Estimating Bismuth Volumetrically.*

By M. M. Pattison Muir, F.R.S.E., Prælector in Chemistry, Caius College, Cambridge.

1. When a saturated solution of oxalic acid is added to a solution of bismuth in nitric acid, a white crystalline precipitate slowly forms this precipitate, according to Souchay and Lenssen (*Ann. Chem. Pharm.*, cv, 245) is normal bismuth oxalate, $Bi_2 3C_2O_4$ + aq.

This reaction appeared to afford a mean whereby bismuth might be accurately and readily determined. If the oxalate were produced under conditions which might be realised without too much difficulty, and if this oxalate were of constant composition, every requisite of an accurate volumetric process would be fulfilled.

2. I carried out several experiments, using a solution of bismuth in a small excess of nitric acid; precipitating with a saturated solution of oxalic acid; washing by decantation; dissolving in warm dilute sulphuric or hydrochloric acid; titrating with standard permanganate; and calculating on the assumption that three molecules of oxalic acid found corresponded with two atoms of bismuth thrown down as oxalate. The results were not, however, very satisfactory, the amounts of bismuth found being generally too low, and the numbers exhibiting considerable discrepancies.

3. Souchay and Lenssen (*loc. cit.*), have shown that the action of hot water upon normal bismuth oxalate results in the production of a basic oxalate having the composition $Bi_2O_3.2C_2O_3$ + aq.

This oxalate is stable; it is only slightly soluble in nitric acid. By taking advantage of the production of this basic oxalate I thought it would be possible to estimate bismuth accurately.

To a measured volume of a solution of a weighed quantity of bismuthous oxide in nitric acid, an excess of a saturated solution of oxalic acid was added; the supernatant liquid was poured off from the precipitate, which soon settled to the bottom of the vessel; the precipitate was boiled with successive small quantities of water, until the decanted liquid ceased to exhibit an acid reaction; the residue was dissolved in dilute hydrochloric acid; and standardised permanganate of potassium was run in—the liquid being maintained at a temperature of 60° or so—until a permanent pale pink colour was produced. The results obtained were accurate, and showed no discrepancies. I quote a few:—

(1.) 50 c.c. bismuth-solution = 0·28404 gram Bi : used 51 c.c. standard permanganate = 0·17008 gram $H_2C_2O_4.2H_2O$ = 0·28348 gram. Bi. difference = — ·00056 gram.
(2.) 50 c.c. bismuth-solution = 0·28404 gram. Bi. : used 50·7 c.c. permanganate = 0·28182 gram Bi. difference = — ·00222 gram.
(3.) 10 c.c. bismuth-solution = 0·056364 gram Bi : used 10·2 c.c. permanganate = 0·056697 gram Bi. difference + ·000333 gram.

The calculation is based on the assumption of the accuracy of the formula assigned by Souchay and Lenssen to the basic oxalate of bismuth. I have, by independent analysis, proved the accuracy of their formula. One molecule of oxalic acid found corresponds with one atom of bismuth.

4. The solution containing bismuth must be free from hydrochloric acid as the basic oxalate is readily soluble in that acid. A large excess of nitric acid must also be avoided. Oxalic acid must be added in considerable excess. If the precipitate be thoroughly shaken up with the liquid, and the vessel be then set aside, the precipitate quickly settles, and the supernatant liquid may be poured off through a filter in a very short time. I find that if the precipitate be boiled for 5 or 10 minutes with successive quantities of about 50 c.c. of water, it is quickly transformed into the basic salt. So soon as the supernatant liquid ceases to show an acid reaction, the transformation is complete. It is well to employ a solution of permanganate so dilute that at least 50 c.c. are required for the titration. The basic oxalate may be dissolved in dilute sulphuric acid in place of hydrochloric; it is more soluble, however, in the latter acid; if the solution contains but little hydrochloric acid there is no danger of chlorine being evolved during the process of titration.

5. In applying this process to the estimation of bismuth in solution containing other metals, it is necessary if the solution contain substances capable of acting upon, or of being acted on by permanganate, to separate the bismuth from the other metals present. This is easily done by precipitating in a partially neutralised solution with much warm water and a little ammonium chloride. The precipitate must be dissolved in nitric acid, and the liquid boiled down once or twice with addition of the same acid in order to expel all hydrochloric acid, before precipitating as oxalate. The liquid should contain just sufficient nitric acid to prevent precipitation of the basic nitrate before oxalic acid is added.

6. The failure of those experiments in which I sought to determine bismuth after precipitation as normal oxalate, is evidently to be traced to the partial decomposition of the normal salt by the wash-water with the production of varying quantities of basic oxalate. My own

experiments have convinced me that the normal oxalate very readily undergoes partial decomposition by contact even with cold water.

7. Of the various methods which I have devised for the volumetric estimation of bismuth, I regard the oxalate method as the most generally applicable. No special standard solution is required, as permanganate solution is in constant use where volumetric analysis is practised; the process is simple and accurate, and may be quickly carried out: bismuth is readily separated from other metals and brought into a condition suitable for estimation by this method.

X.—*On Cuprous Chloride and the Absorption of Carbonic Oxide and Hydrochloric Acid Gas.*

By J. W. Thomas.

Some years ago I noticed considerable irregularity in the determination of carbonic oxide by absorption when using the reagent in the liquid form, simply passing the solution by the usual pipette into the laboratory tube or absorption tube, and I came to the conclusion that the incorrectness of my determinations was due to the strength of the acid solution of cuprous chloride which I employed. On trying the cuprous chloride solution, supersaturated with ammonia, concordant results were obtained, and I have since used the re-agent in this form.

Although the percentage of carbonic oxide (CO) in a gaseous mixture is very accurately determined by explosion with oxygen, the direct determination of the same by absorption is very important when it is required to know the constituents of a gas of unknown composition containing various carbon compounds. In order therefore to discover the reason of the irregularity in the absorption of CO by cuprous chloride, I undertook the experiments the results of which I now have the honour of submitting to the Society.

The method recommended for making cuprous chloride (Cu_2Cl_2) for use in gas analysis (Sutton's Volumetric Analysis, p. 285) is to strongly acidulate a saturated solution of cupric chloride ($CuCl_2$) with hydrochloric acid (HCl), and place the solution in a bottle with copper filings or turnings, leaving it until the liquid is colourless. This end can be accomplished by adding almost any quantity of acid, provided the solution is allowed to stand for a sufficient time.

In endeavouring to find a more expeditious method by which a Cu_2Cl_2 solution could be made and the acid strength known comparatively, I

tried that of Wohler (Watt's Dict., 1st sup., p. 493), dissolving the cuprous chloride in hydrochloric acid of known strength. Although a good method, the process is tedious. By accident, when trying some experiments with hydrochloric acid of different but unknown strengths upon $CuCl_2$, I succeeded in making a colourless solution of Cu_2Cl_2 instantly, but although I have tried many times since I have not succeeded in doing it again. The result of successive trials brought out the following method, which is very expeditious, although little more than an old method perfected. A long, narrow stoppered bottle, holding about 4 ozs., is filled *three parts* full with closely-packed copper turnings, previously boiled in caustic soda to remove grease. Introduce 6 grams of the ordinary hydrous cuprous chloride, and add 20 c.c. of hydrochloric acid (ordinary strong acid, mur. pur.), and shake for a minute until the cupric chloride is dissolved and forms the black cuproso-cupric chloride, then add 10 c.c. of water and let it run into the bottle slowly so as to float on the surface of the acid liquid; replace the stopper of the bottle and give the latter a violent shake, when the solution becomes colourless instantly, and entirely converted into cuprous chloride, a large quantity of the white compound being deposited. This is a striking illustration of the action of water in breaking up unstable chemical compounds. The colourless solution, which is very strongly acid, is saturated with cuprous chloride, and after the addition of a further 30 c.c. of water, is ready for use (sol. B). The following is another good method for making cuprous chloride rapidly, the operation being conducted as before in a bottle three parts filled with clean and, in this instance, dry copper turnings closely packed. Six grams of anhydrous cupric chloride is placed in the bottle and 20 c.c. of the strongest hydrochloric acid added; on shaking for a minute or two the liquid will become colourless and the acid saturated with cuprous chloride (sol. A).

For the purpose of finding the best strength of cuprous chloride solution for use in gas analysis, and the most accurate method of using it, I prepared some pure carbonic oxide from formic acid. Solution A and B, and in fact any solution of cuprous chloride in hydrochloric acid, no matter how concentrated or reasonably dilute, absorbs carbonic oxide with facility, and the irregularity in the estimation of CO by absorption is due to the subsequent treatment of the solution with potash or soda to neutralise the free hydrochloric acid. When solution A or B, or one of intermediate or weaker strength was used, the absorption of carbonic oxide was rapid, especially if the absorption tube was agitated: when, however, a solution of potash was added, notably if passed from a quick-delivering pipette, a considerable evolution of gas takes place. Much of the gas so liberated is carbonic anhydride, expelled from the potassium carbonate present in the potash-solu-

tion by the free hydrochloric acid, but I invariably found that some carbonic oxide was set free, and that the quantity liberated depended upon the manner in which the KHo was added. If the potash (a saturated solution was employed) was passed up slowly and allowed to form a stratum underneath the acid solution (separated by a film of cuprous hydrate) and, when it was added in excess, the absorption tube is briskly and suddenly agitated, as much as 63 per cent. of the carbonic oxide can be set free and will remain unabsorbed. The carbonic acid liberated is of course absorbed when the caustic alkali is in excess. When the potash is slowly added and the mercury is allowed to drop through the liquid, or the absorption tube is feebly agitated, the quantity of CO liberated is very much decreased, and it is possible to reduce it to 4 per cent.; the reaction is not, however, very controlable. I next tried whether the liberation of carbonic anhydride caused a similar evolution of carbonic oxide, and, to this end, removed as much carbonic anhydride as possible from the potash solution by quicklime, but did not obtain any better results. Potash-solution of varying strengths was tried in order to see if the saturated solution was too concentrated, but the results obtained were very similar, carbonic acid being liberated according to the manner in which the acid solution was neutralised, and the carbonic oxide liberated in 6 experiments amounted to 42·6 per cent., 37·4 per cent., 14·4 per cent., 5·2 per cent., 3·8 per cent., and 23·8 per cent. I endeavoured to liberate as much as possible in the two first experiments.

Apart from the action of potash, the absorption of carbonic oxide by cuprous chloride, although very rapid at first until from 90 to 95 per cent. has been taken up, is by no means complete under half an hour if left at rest, or 15 minutes if well agitated, as the last traces are very slowly absorbed, more especially when mixed with a large volume of hydrogen, which gas appears to retard the absorption of carbonic oxide more than any which I have tried. Although the hydrochloric acid solution of cuprous chloride may be used to detect the presence of carbonic oxide, it cannot be relied upon for a quantitative determination when potash or soda is used subsequently to neutralise the free hydrochloric acid.

The above experiments relate only to the use of cuprous chloride in the liquid form in apparatus of the Frankland and Ward model, and have little bearing on the absorption of that gas by a papier machié ball saturated with the re-agent, and the acid vapour subsequently removed by a potash ball. I found, however, that by allowing the cuprous chloride solution to wet the sides of the absorption tube and the potash ball afterwards to come in contact with the liquid, that the accuracy of the absorption, even by this method of procedure, was perceptibly impaired.

The method which I long employed was to add ammonia to the cuprous chloride solution until it was strongly alkaline and the precipitate at first formed was redissolved, and after the absorption of carbonic oxide had taken place, to add very dilute sulphuric acid until the blue colour of the absorbent was nearly destroyed. There is, however, a liability to introduce error by proceeding in this manner, especially if the hydrochloric acid solution of cuprous chloride is strongly supersaturated with ammonia, and if the latter contains much carbonate, on account of the carbonic anhydride which would be disengaged by the sulphuric acid and the risk of adding too much of the latter to set hydrochloric acid free. I have recently made some experiments with a view of using the ammonio-cuprous chloride solution in a form which shall be sufficiently neutral to dispense with the necessity of employing any re-agent to remove the vapour of ammonia.

The following method was found to give very concordant results when tried on the same sample of a gaseous mixture. A small pipette (straight) is required, having a long narrow point with an orifice smaller than a wash-bottle jet. Some ammonia (strength one NH_3, ·880, to one of H_2O) is sucked into the pipette and a little of the cuprous chloride solution (B) is poured into a small porcelain crucible or a test-tube on foot, cut short, and stirred with the pipette containing ammonia. As soon as the slightest shade of blue remains permanent, on stirring, fill the usual bent pipette with the solution and introduce the latter into the absorption tube *at once*, the gas being previously ready for the absorption. The ammonia when added to the hydrochloric solution of cuprous chloride forms ammonio-cuprous chloride (in addition to ammonium chloride) which soon separates in the form of very minute transparent crystals, and only a very little, of what appears to be a hydrate, is formed, and the slightest excess of ammonia over that required to neutralise the acid is indicated by the liquid assuming a blue colour. It is well known that when ammonia is added in excess to a colourless solution of cuprous chloride, in the absence of oxygen, the solution remains colourless, but if the cuprous chloride solution is exposed to the air for a few seconds, even some of the cuprous chloride is oxidised, and as quickly converted by the free acid into cupric or cuproso-cupric chloride, which gives a blue colour with ammonia as soon as the free acid is neutralised. By proceeding thus there will be no free ammonia to pervade the gas (the first blue colour being due to ammonio-cuproso-cupric chloride), and consequently no necessity to add acid subsequently, and although much of the copper compounds are precipitated, the re-agent absorbs carbonic oxide nearly as well as the hydrochloric acid solution of cuprous chloride. It is unnecessary to give details of the experiments made, but I may mention that they

were tried on mixtures of carbonic oxide and hydrogen, carbonic oxide and marsh-gas, carbonic oxide and ethane, and coal gas (free from carbonic anhydride and oxygen), and in all instances gave very good results, but the absorption is not complete under half an hour, unless the vessel is briskly agitated.

A large volume of a mixture of hydrogen and marsh-gas was measured and then transferred over the ammonio-cuprous chloride solution prepared as above in order to see if the pressure of the gas varied, the difference in the two readings was ·03 per cent. The hydrochloric acid solution of cuprous chloride (B) answers well, but it should be kept colourless, and to this end the copper turnings must always be above the liquid and the bottle well stoppered, else the solution soon becomes less acid, owing to the formation of further quantity of cuprous chloride, through oxidation and subsequent reduction.

Since the above was written I have made further experiments, with a view of using phosphoric acid in the place of sulphuric acid for neutralising an alkaline (NH_3) solution of cuprous chloride, and I have also endeavoured to arrive at some method of neutralising the acid solution of cuprous chloride by other reagents than potash and soda. Phosphoric acid does not appear to liberate hydrochloric acid from ammonium chloride in the cold, and only traces of hydrochloric acid are given off when a concentrated solution of ammonium chloride is boiled with phosphoric acid.

The free hydrochloric acid in an acid solution of cuprous chloride is neutralised by phosphate of ammonia, phosphate of soda, oxalate of ammonia, oxalate of soda, sulphate of soda, sulphate of ammonia, and alkali tartrates.

It is stated (Sutton's Volumetric Analysis, p. 367) that sodic phosphate and sodic sulphate owe their absorbent powers (for HCl gas) to the water of crystallisation which they contain, and in Watts's Dict. of Chem., i, 282, "the ball of sulphate of sodium is recommended to be large, else, if much HCl gas be present, the sulphate of sodium is apt to become deliquescent." I find that phosphate of soda and sulphate of soda do not absorb HCl gas by virtue of their water of crystallisation, but by giving up half their Na to form acid salts and sodium chloride. When HCl is added to a saturated aqueous solution of sodic phosphate at the boiling temperature, the whole of the acid combines with the sodium of the phosphate and forms sodium chloride, providing there be two equivalents of sodium to one of HCl in the solution.

From experiments, it appears probable that in the presence of water at the ordinary temperature hydrochloric acid displaces all the sodium in hydric-disodic phosphate. Either sodic sulphate or disodic phos-

phate may be used to neutralise the free hydrochloric acid in the solution of cuprous chloride after the absorption of carbonic oxide, but although a saturated solution of the former contains more sodium, a solution of the latter does not apparently contain free hydrochloric acid when the quantity of that acid present is nearly equivalent to the total sodium. A saturated solution (aqueous) of ammonium sulphate is, however, the best adapted for neutralising the free acid in a cuprous chloride solution, as this salt is very soluble in water, and also possesses the advantage of holding the cuprous chloride in solution without destroying its absorbent properties, so that the solution of ammonium sulphate might, if required, be added to the acid solution of cuprous chloride before introducing it into the laboratory tube. The hydrochloric acid solution of cuprous chloride (B) requires about 80 per cent. of its volume of a saturated solution of sodium sulphate to neutralise the hydrochloric acid, but it is best to add volume for volume. Perfectly dry ammonium sulphate absorbs HCl gas very readily. When a saturated solution of sodium sulphate or disodic phosphate is added to a HCl solution of cuprous chloride after the absorption of carbonic oxide, no carbonic oxide is liberated, but a white crystalline precipitate of cuprous chloride falls down and is afterwards partly dissolved in the sodium chloride formed. If, after a saturated solution of disodic phosphate is added, the tube containing the cuprous chloride, &c., is allowed to stand over mercury for several days, the undissolved cuprous chloride becomes converted into cupric phosphate by the reduction probably of orthophosphate to pyrophosphate, but no carbonic oxide is liberated.

When a gaseous mixture containing hydrochloric acid is analysed in an apparatus on Dr. Frankland or Prof. M'Cleod's model, a few drops of a saturated solution of sodium sulphate may be used to remove hydrochloric acid gas, and potash and pyrogallic acid may be subsequently introduced to absorb carbonic anhydride and oxygen without washing out the laboratory tube, but owing to the moisture which invariably remains in the eudiometer the result will be much more accurate if the absorption of the hydrochloric acid gas is conducted in an ordinary absorption tube, and the remainder of the analysis done in the apparatus mentioned. The experiments relating to the action of hydrochloric acid upon sodium sulphate, &c., will be described in another paper.

XI.—*On Citric Acid as a Constituent of the Juice of Unripe Mulberries.*

By C. R. Alder Wright, D.Sc., and Geo. Patterson.

Through the kindness of Dr. Hardwicke, coroner for Middlesex, we obtained a quantity of the juice of mulberries grown in his garden at Hendon. The fruit did not appear to ripen this year as fast as usual, so that, before it was fully ripe, an early frost almost stripped the tree of leaves, leaving bushels of berries not quite fit for eating. The juice of these was expressed, and constituted a somewhat turbid light brown fluid of very acid taste. On keeping in a loosely corked phial, it became mouldy on the top, and developed a small quantity of alcohol.

On qualitative examination, it was found to contain a considerable amount of mucilaginous matter, precipitable by addition of an equal volume, or rather more, of strong alcohol. The filtrate from this, when boiled down so as to expel the alcohol, and neutralised with ammonia, gave no precipitate with calcium chloride in the cold, but on boiling for half an hour threw down a sandy calcium salt. The concentrated filtrate from this (containing excess of calcium chloride and rendered alkaline by ammonia) deposited no more precipitate on further boiling, but on addition of alcohol an amorphous lime-salt was thrown down. From these observations it appears that whilst oxalic and tartaric acids were absent, or present in insignificant quantity only, citric acid was present to a considerable extent, and apparently also malic acid. A volatile acid, presumably acetic acid, was also found in minute quantity. Fehling's solution was easily reduced on boiling.

To determine approximately the citric acid, a known quantity of juice was boiled with ammonia and a recently boiled and filtered mixture of calcium chloride and ammonia, until no further precipitate was occasioned in the filtered liquid on further boiling; the precipitated calcium citrate was collected and washed with a minimum of water till the washings were free from chlorine, then dried, and determined as calcium carbonate by ignition, and treatment of the residue with ammonium carbonate. The filtrate was treated with twice its volume of alcohol, and the precipitated gelatinous lime-salt collected, washed with 60 per cent. spirit, and weighed as carbonate. The ash left on incineration was dissolved in hydrochloric acid and treated with ammonia, whereby a precipitate mainly consisting of phosphate of calcium was thrown down; the lime in the filtrate from this was determined as oxalate, and the potash in the filtrate by platinic chloride after evaporation to dryness and ignition.

The following numbers were obtained:—

		Grams per litre.
Citric acid,	25 c.c. gave 0·524 $CaCO_3$ = 0·6707 $C_6H_8O_7$ =	26·83
Malic acid,	„ 0·146 „ = 0·1956 $C_4H_6O_5$ =	7·82
Glucose,	25 c.c. reduced Cu_2O containing 0·1220 Cu = 0·0685 glucose =	2·74
Ash,	25 c.c. gave 0·2350 total residue, of which	
	0·0330 was phosphate of lime, &c., precipitated by NH_3 ..... = 1·32	
	0·0140 was $CaCO_3$ ..... 0·56	
	0·0815 „ K_2CO_3 ..... 3·26	
	0·1065 „ Na_2CO_3, silica, and matter undetermined ..... 4·26	
	0·2340	9·40
Other constituents, mucilage, pectin, &c., &c.		23·37
Total solids (25 c.c. gave 1·754 grams after drying for about 24 hours at 100°, till almost constant in weight)..... =		70·16
Volatile acid (reckoned as acetic acid)		0·27
Total acidity, determined by titration and reckoned as anhydrous citric acid, $C_6H_8O_7$		28·14

In order to confirm the presence of citric acid, the juice was boiled with marble powder, and the organic lime-salt formed washed and decomposed by sulphuric acid. In this way citric acid was readily obtained. The calcium salt of the acid thus isolated was prepared by neutralising with ammonia, adding a filtered boiled mixture of calcium chloride and ammonia, boiling, and well washing the sandy precipitate. After drying at 100° till constant, the following numbers were obtained:—

0·3950 gram dried at 150—160° lost 0·0330 =	8·35	per cent.
Calculated for $(C_6H_5O_7)_2Ca_3,2H_2O$..... =	6·74	„
0·361 gram of dried residue gave 0·293 $CaSO_4$ ..... Ca =	23·87	„
Calculated for $(C_6H_5O_7)_2Ca_3$ ..... =	24·09	„

According to Warington (this *Journal*, 1875, 925), citrate of calcium dried at 100° contains 5·91 to 7·68 per cent. of water of crystallisation, or approximately $2H_2O$. According to some text-books, however, the salt when dried at 100° is $(C_6H_5O_7)_2Ca_3,H_2O$.

It results from these numbers that whilst unripe mulberry juice is not as rich in citric acid as lemon and lime juice (which contain 8 to 12 ounces per gallon, or 50 to 75 grams per litre of crystallised acid, or 46 to 68 grams per litre of anhydrous acid, $C_6H_8O_7$—Warington,

loc. cit.), it is still sufficiently rich to be a notable source of that acid. From this circumstance, and the presence of considerable quantities of potash, it seems probable that the juice of imperfectly ripe mulberries may be found to be valuable as an antiscorbutic, and as a substitute for lime juice.

XII.—*On the Hydrocarbons obtained from the* Pinus Sylvestris, *with Remarks on the Constitution of the Terpenes.*

By William A. Tilden, D.Sc. (Lond.).

I. *Russian Turpentine Oil.*

Some months ago, by the kindness of Dr. Armstrong, I received a quantity of Russian turpentine oil, with the information that it would distil chiefly between 168° and 180°, that is at a temperature considerably above the boiling point of the terpenes of ordinary American and French turpentine.

The sample contained a small quantity of acetic acid and empyreumatic products, and there can be no doubt, therefore, that this oil is obtained, not from the natural exudation from the living tree, but as a bye-product during the distillation of the wood for the purpose of preparing tar, as practised extensively in the north of Europe. According to Hanbury and Flückiger (*Pharmacographia*) the trees used for this purpose are chiefly the *Pinus sylvestris* and *Pinus Ledebourii*.

The Russian turpentine oil as it came into my possession had the specific gravity 0·8682, and 100 mm. of the liquid, tested by Wild's instrument, using the soda flame, were found to rotate the polarised ray about 17° to the right. It has a yellowish colour, and a peculiar pleasant odour, quite distinct from that of common turpentine oil.

After shaking with solution of caustic soda to remove acetic acid and creosote, the oil was submitted to fractional distillation, the fractions ultimately obtained of nearly constant boiling point, being finally distilled once or twice from sodium. There are four principal ingredients in this turpentine—

1. The most volatile constituent is a terpene boiling at the same temperature as australene (from American oil), but its action on the polarised ray is much greater than that of australene. 100 mm. give a rotation of + 23·3°. There can be no doubt, however, that it is identical from a chemical point of view with australene, since it

behaves in the same manner as that hydrocarbon when acted upon by nitrosyl chloride gas.

This terpene constitutes 10 to 15 per cent. of the turpentine oil.

2. A second terpene present in Russian turpentine oil is an entirely different substance.

After a most tedious series of fractionations and examination of the products, I have come to the conclusion that the pure hydrocarbon boils under ordinary atmospheric pressure at 171°, or thereabouts. A considerable quantity of it, boiling at 171° to 171·5°, was collected. It possesses a characteristic odour. 100 mm. rotate the polarised ray 17° to the right. Its specific gravity was 0·86529 at 15°. It gave by combustion 88·09 per cent. of carbon, and 12·14 of hydrogen, and by Hofmann's process a vapour density =65·8 (H = 1). The formula $C_{10}H_{16}$ requires 88·23 per cent. of carbon, 11·76 per cent. of hydrogen, and vapour density 68.

This terpene occurs in the turpentine oil to the extent of about two-thirds of its volume.

The product I have just described is, I believe, as pure as it is possible to get it. Nevertheless, I think it contains traces of cymene, a hydrocarbon of which this turpentine contains a considerable quantity, and from which it would be very difficult to separate it completely, in consequence of their boiling points lying so close together.

3. Cymene was isolated by the usual process from the two fractions boiling at 172—173° and 173—175°. These were mixed together. A portion of the mixed liquid was oxidised by chromic acid, when it gave about 3 per cent. of a mixture of toluic and terephthalic acids. The rest was divided into two portions.

50 c.c. were cooled by ice and salt, and then mixed very gradually with more than an equal bulk of oil of vitriol. After standing for twenty-four hours the mixture was diluted, and from the separated oil a quantity of cymene was obtained equal to about $7\frac{1}{2}$ per cent. by weight of the liquid operated upon.

The second part of this liquid, consisting as it did mainly of the new terpene, was submitted to the action of bromine in order to remove if possible two atoms of hydrogen and convert it into cymene. In order to moderate the action of the bromine upon the hydrocarbon, the latter was diluted with about twice its bulk of chloroform. 30 c.c. of terpene and 60 c.c. of chloroform were mixed, and the liquid cooled to $-10°$ before the bromine (rather less than 28 grams) was gradually added. The resulting nearly colourless liquid was distilled, the chloroform being collected separately, and the distillation carried on till the thermometer went up to 240°, and only a few drops of black liquid remained. Much hydrobromic acid was evolved throughout the operation. The liquid was returned to the flask and redistilled five or six

times till the fuming ceased. It was then distilled several times from sodium. About $14\frac{1}{2}$ grams were collected, corresponding to $56\frac{1}{2}$ per cent. by weight of the mixed hydrocarbons taken.

The cymene was in both these experiments recognised by smell, optical inactivity, boiling point, and oxidation products.

In order to represent the amount of cymene produced by the splitting up of the dibromide, the quantity which was obtained in the first experiment, and represents pre-existent cymene, must be subtracted from the quantity obtained in the second: that is, $56\frac{1}{2}—7\frac{1}{2} = 49$ per cent., or nearly half its weight.

I have not succeeded in obtaining from the liquid, which I believe to be the nearly pure terpene, any solid hydrochloride by the action of hydrochloric acid gas upon the hydrocarbon alone, or upon its solution in ether.

Nitrosyl chloride gas passed into the hydrocarbon, whether pure or diluted with chloroform or with alcohol, produces no crystalline nitrosochloride as in the case of all other terpenes hitherto examined. After passing the gas into a mixture of the terpene with chloroform and allowing the solution to evaporate spontaneously, a few scaly crystals were deposited. These, when collected and dried by pressure, were found to be very easily soluble in rectified spirit, and the solution when set aside deposited nothing but oily drops.

4. The presence of cymene in the Russian oil has been already proved.

5. The oil contains small quantities of viscid hydrocarbons boiling at high temperatures.

Within the past few months an examination of Swedish turpentine oil has been published by A. Atterberg (*Deut. Chem. Ges. Ber.*, x, 1202).

He finds in this oil two terpenes. The one boils at 156·5—157·5°, and has the specific rotatory power + 36·3°. The other is said to boil at 173° to 175°, with a specific rotatory power = + 19·5°, and a specific gravity ·8612 at 16°. The latter is called by Atterberg "sylvestrene." I believe it to be identical with the terpene I have described, partly on account of their close agreement in boiling point and rotatory powers, partly because they are almost certainly derived from the same source. I have not, however, been able to obtain a crystallised dihydrochloride in the manner described by Atterberg.

II. *Oleum foliorum Pini sylvestris.*

Under this name an oil is prepared for use in medicine by distilling the leaves of the Scotch fir with water. I believe it to be identical with the "Fir-wool oil" imported from Germany.

The specific gravity of the sample I examined was 0·8756, and 100 mm. of the liquid turn the plane of polarisation $5\frac{1}{2}°$ to the right. When distilled it began to boil at 80°, owing, as I afterwards found, to the presence of a small quantity of alcohol.

The temperature went up rapidly to near 165°, below which point about one-fourth of the whole passed over. Between 165° and 175° a distillate was obtained equal to about two-thirds of the original liquid.

By careful fractionation this oil was found to contain, beside small quantities of other bodies, two terpenes corresponding in boiling point with those obtained from Russian turpentine oil.

The first smells like common turpentine, boils at 156° to 159°, and a column of the liquid 100 mm. long rotates the plane of polarisation + 18° 48′. It is, therefore, like australene dextrorotatory, but more strongly so than the usual variety. It possesses, however, the same chemical constitution, for it behaves with nitrosyl chloride in precisely the same manner.

The second terpene, which constitutes about two-thirds the bulk of the oil, boils at 171° or a little above. It is lævorotatory. The rotation per 100 mm. is about − 4°, but this number can be considered only as an approximation, since the liquid with which the determination was made was undoubtedly contaminated with traces of cymene, as well as of another compound present in the oil, and it was found impossible to purify it completely.

This hydrocarbon possesses the same odour and behaves in the same manner towards reagents as the liquid boiling at the same temperature obtained from Russian turpentine. It also has the same specific gravity at 15°, viz., ·86529.

No solid hydrochloride could be prepared by saturating with hydrochloric acid gas and exposing the resulting liquid to spontaneous evaporation, or to a very low temperature in a freezing mixture.

In addition to these two terpenes, the essential oil of the *Pinus sylvestris* contains a small quantity of cymene and of pleasant-smelling liquids of higher boiling point.

III. *Remarks on the Constitution of the Terpenes.*

In discussing this question, several facts must be taken into consideration:

1. From experiments carried out in conjunction with Mr. Shenstone (*J. Chem. Soc.*, 1877, i, 554), I find that the number of isomeric terpenes is certainly very small, and according to my belief, there are amongst the natural terpenes only three isomerides essentially different in chemical constitution. The known varieties of these differ

only in odour, in action on polarised light and other optical properties,* and these differences can be fully accounted for without assuming any but mechanical differences of constitution.

Thus I find that the terpenes from the following sources yield the same nitroso-derivatives. The terpenes themselves boil at 156° to 159°, and have nearly the same density, viz., about 0·860.

Dextro-rotatory.

American turpentine oil.....	Natural order. Coniferæ.
Russian turpentine oil	
Oil of leaf of *Pinus sylvestris*..	

Lævorotatory.

French turpentine oil.....	N.O. Coniferæ.
Oil of sage	N.O. Labiatæ.
Oil of juniper	N.O. Coniferæ.

To these I feel pretty confident may be added the non-rotating hydrocarbon, terebene, which boils at 155—156°, and has the specific gravity 0·860 at 20° (Riban). Like terebenthene, it yields a crystalline monohydrochloride. The semi-hydrochloride which this substance was supposed to form, has been shown by Riban to be a solution of the monohydrochloride in cymene. To the presence of cymene may also probably be ascribed my failure to obtain a crystalline nitroso-compound from the terebene upon which I operated.

The second group of terpenes comprises those which boil at or near to 174°, and which have a density somewhat below ·85 at 20°. These all yield the same nitroso-substitution compounds having the same melting point and crystalline form. They are obtained from the following volatile oils:—

Dextrorotatory.

Oil of sweet orange peel	Natural Order Aurantiaceæ.
Oil of bergamot	
Oil of lemon	
Oil of caraway	N. O. Umbelliferæ.

The third class comprises the two terpenes of higher boiling point described in this paper as derived from

Russian turpentine	N. O. Coniferæ.
Oil of leaf of *P. sylvestris*	

* The slight differences observed in density and boiling point in the several members of the same group of terpenes are probably in the main owing to the fact that in very few cases have the substances operated upon been in a pure state.

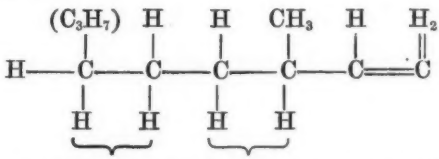
With the former of these, as already stated, Atterberg's "sylvestrene" will, I believe, be identified. They all boil at 171—175°, and have a specific gravity higher (·865 at 15°) than that of any of the others, whilst they yield no crystalline monohydrochloride or nitroso-chloride.

2. All known terpenes yield, by the action of bromine, one and the same cymene, and that α-cymene, the constitution of which is admitted to be that of methyl-propyl-benzene, probably containing *iso*-propyl.

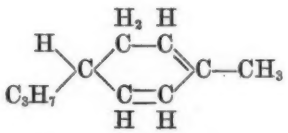
3. Terpenes are almost entirely broken up by oxidation into carbonic and acetic acids, and yield neither toluic nor terephthalic acid when pure. In those cases in which minute quantities of these acids have been obtained, their production is to be attributed to the presence of traces of cymene in the terpene operated upon. This has been already pointed out by Dr. C. R. A. Wright, and I agree with him upon this point. The production of toluic and terephthalic acids by oxidation of terpin (Hempel, *Liebig's Annalen*, clxxx, 71) seems to me to throw no light upon the question. I shall refer to this again presently. Terebic and terpenylic acids, from what is known of them, are not benzene derivatives. And, lastly, it must not be forgotten that considerable quantities of oxalic acid are always produced when turpentine is oxidised by nitric acid.

4. Cymene cannot be made to combine with hydrogen, so as to produce a terpene.

5. Terebene has been obtained from diamylene by removal of four atoms of hydrogen. Von Richter's formula for diamylene is represented as follows:—



It was the consideration of this last fact which chiefly led me to observe that Oppenheim's formula for turpentine, which is identical with the formula for terebene proposed by v. Richter, is not the only nor even the most probable formula which presents itself for these bodies. That formula represents turpentine as containing the benzene ring of six carbon atoms, as being in fact cymene with two atoms of hydrogen added.

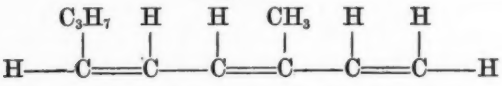


This formula agrees with my hypothesis that there exist but three

isomeric terpenes, assuming that the propyl group is always the same. It also agrees with the fact that cymene can be obtained from turpentine by the removal of two units of hydrogen and two of bromine from the dibromide. But it is very difficult to reconcile with the fact that the same cymene is obtained from all the known terpenes, the isomerism of which must be explained, according to this hypothesis, by the assumption that the hydrogen symbols change their position in the formula. It is also difficult to explain by this formula why, as I maintain, toluic and terephthalic acids are not obtained by the action of oxidising agents upon the terpenes.

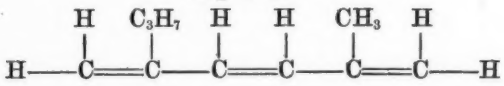
The formula which I propose for discussion is derived very simply from the formula for diamylene; for on removing the two pairs of hydrogen symbols, bracketed together in the formula written above, we come to the following expression:—

Terpene α.

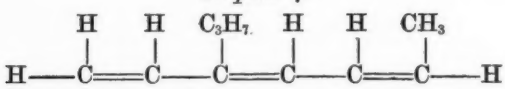


It is now clear that this admits of two other modifications, as represented below, viz.:—

Terpene β.



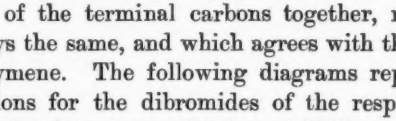
Terpene γ.

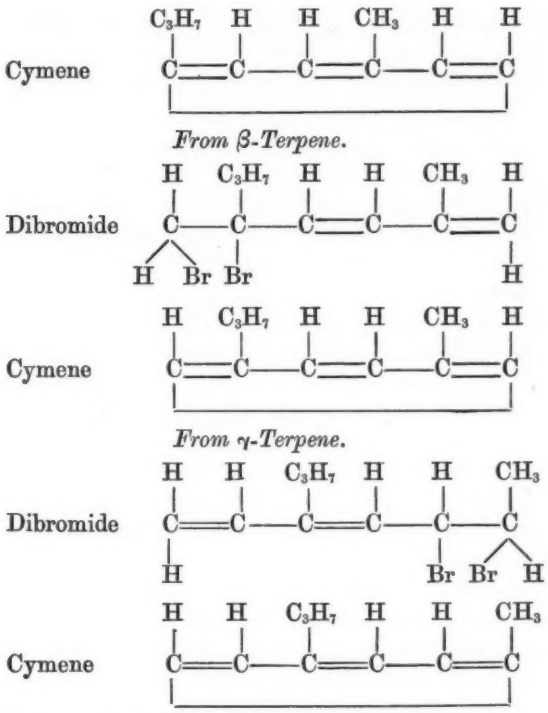


The isomerism arises, therefore, from the varying positions of the propyl and methyl groups upon this chain of carbon. So long as these two radicles maintain their distance from one another in the formula, the removal of one hydrogen symbol from each end of the chain and the linking of the terminal carbons together, result in a formula which is always the same, and which agrees with the received formula for ordinary cymene. The following diagrams represent the most probable expressions for the dibromides of the respective terpenes, and their conversion into cymene by loss of 2HBr.

From α-Terpene.

Dibromide





From β-Terpene.

From γ-Terpene.

These three formulæ for cymene are evidently identical.

Hempel has found that terpin hydrate yields, when oxidised, toluic and terephthalic acids, and hence concludes that the production of these acids by oxidation of ordinary turpentine cannot be wholly attributed to the existence of cymene or other impurities in the turpentine. Now when terpin hydrate is heated with diluted nitric acid, the first effect in the removal of the elements of water and production of terpinol, which, if it really has the formula usually assigned to it, namely, $C_{20}H_{34}O$, or $C_{20}H_{33}(OH)$, is a condensation product. Since it contains but one oxygen-atom, and that supposed to be in the form of hydroxyl, it must evidently be generated by the union of carbon to carbon in some way at present unknown. On the other hand, there is the not improbable suggestion put forward by Gerhardt, that terpinol may be a hydrocarbon, an isoterpene. This supposition derives support from the fact, that the terebene semi-hydrochloride, $C_{20}H_{33}Cl$, to which terpinol was supposed to correspond, does not exist.

Whatever be the real nature of terpinol, my object in referring to it is only to point out that the products of its oxidation must not be assumed without further evidence to be the same as those of a terpene.

I have only further to say, with regard to this question, that the formulæ proposed in this paper for the terpenes are brought forward with the utmost diffidence. But although I do not insist upon them, it seems to me that, in view of the dead-lock at which we have arrived in regard to the question of the constitution of these compounds, the time has come when we may fairly test the capacities of some hypothesis different from that which has hitherto chiefly found favour.

From the terpenes to camphor is a comparatively short step; and although I have no experiments of my own to offer, I cannot forbear a few words upon the subject.

The following facts seem to have been established:—

1. Camphor, identical with ordinary camphor in all but rotatory power, has been obtained by Riban by oxidising the lævogyrate camphene from French turpentine oil. Camphor is also said to have been formed by oxidising turpentine by permanganate (Berthelot).

2. Camphor, by losing the elements of water, yields ordinary cymene identical with that obtained from the terpenes.

These two circumstances seem to connect camphor with turpentine, and at first sight it would appear that the grouping of the carbon symbols must be the same in the formulæ of the two compounds. But although I have represented the terpenes as consisting of an open chain of carbon, I feel disposed to consider camphor as a benzene or cymene derivative, and chiefly for the following reasons:—

3. Camphor yields substitution-derivatives with comparative ease. Thus the following compounds have been obtained:—

Bromo-camphor, $C_{10}H_{15}BrO$.
Chloro-camphor, $C_{10}H_{15}ClO$.
Nitro-camphor, $C_{10}H_{12}(NO_2)_4O$.

4. Sodium camphor, treated with carbonic anhydride, yields the sodium salt of camphocarbonic acid, a compound which is easily resolved again into CO_2 and camphor. This reaction is parallel to the production of salicylic acid from phenol.

$$C_{10}H_{16}O + CO_2 = C_{10}H_{15}O.COOH$$
$$C_6H_6O + CO_2 = C_6H_5O.COOH$$

5. By the action of nitric acid, camphor yields, amongst other products, a large quantity (more than half its weight) of camphoric acid, which contains as many C and H atoms as camphor.

6. By loss of H_2, camphor is converted into carvacrol.

These last characteristics, it may be observed, are unlike those of ketones in general, a class of compounds to which camphor, on account of its relations to borneol, is very commonly referred.

XIII.—*On the Luminosity of Benzol when burnt with non-luminous Combustible Gases.*

By E. Frankland, F.R.S., and L. Thorne, Jodrell Scholar.

As early as the year 1852 it was pointed out by one of us that hydrogen, carbonic oxide, and marsh-gas practically contribute nothing to the light of coal-gas, and that the only constituents of this gas having any substantial value as light-giving agents are those hydrocarbons which combine with fuming sulphuric acid.* The chief of the luminiferous hydrocarbons are benzol, ethylene, propylene, butylene, and acetylene; but although a knowledge of the intrinsic individual luminosity of these and other similar bodies is of very great importance in connection with the subject of artificial light, no successful attempts have yet been made to determine it. We have therefore endeavoured to supply the necessary data, and the following pages contain the results of our experiments upon benzol. They will be followed by a similar series upon each of the other chief illuminating constituents of coal-gas.

All our attempts to determine the illuminating power of benzol when burnt alone were futile, on account of the extreme difficulty of obtaining a smokeless flame by the combustion of the pure hydrocarbon. In our efforts to evercome this difficulty we were most kindly assisted by Mr. Albert Silber, who constructed for us several lamps specially designed to consume this liquid; nevertheless, as the utmost light obtainable without smoke, even with these lamps, did not exceed that of one candle, we were compelled to abandon the attempt as hopeless, and to confine our experiments to the determination of the luminous effect of benzol vapour when diffused in hydrogen, carbonic oxide, and marsh-gas. The illuminating power of benzol, as thus determined, is probably a more trustworthy guide to the value of this compound in coal-gas than would have been any direct determinations with the liquid alone, had such been possible. Moreover, these experiments with benzol vapour have brought to light some points of considerable interest in connection with the relative fitness for their office of the three non-illuminating gases, or diluents, of coal-gas.

The determinations were made in the following manner:—Each non-illuminating gas to be charged with the vapour of benzol was collected in sufficient quantity in a holder capable of containing 20 cubic feet, and to which a pressure of 8 feet of water from a ball-

* Memoirs of the Manchester Literary and Philosophical Society (2nd Series), vol. x, p. 71.

University of Michigan

cock cistern could be conveniently applied. From this holder the gas was led through a $\frac{3}{16}$-inch tube to a photometric room, where it was received in a floating bell-gasholder of 1 cubic foot capacity, which served to reduce the pressure of the gas delivered from the large holder, so as to bring it within the control of an experimental governor, whence it passed to a test-meter of the usual construction, showing the hourly consumption of gas by observations of one minute's duration. On leaving the meter the gas entered a benzolizer consisting of a brass cylinder $6\frac{1}{2}$ inches long, and 3 inches internal diameter, filled with sponge saturated with pure benzol, and so arranged as to compel the whole of the gas to pass through the sponge. The benzolizer was entirely immersed in a large vessel of water, the temperature of which was maintained constant during the continuance of the experiments.

Each determination of luminosity was the mean of at least ten separate observations. At the close of the photometric readings, and whilst the current of benzolized gas was maintained, a sample was collected for eudiometric determination of the percentage of benzol vapour, which was effected by fuming sulphuric acid in the usual manner.*

A. *Benzolized Hydrogen.*

The hydrogen was prepared from commercial zinc and dilute sulphuric acid, and contained the usual traces of impurities. It is almost needless to say that a flame of it, burning at the rate of 5 cubic feet per hour, possessed no measurable amount of illuminating power. After passage through the benzolizer, the gas was burnt from a fish-tail burner, when the following photometric results were obtained:—

Rate at which hydrogen passed through meter, 4·95 cubic feet per hour.

Temperature of water in which benzolizer was immersed.....	14·8° C. (58·6° F.).
Temperature of room.....	16·0° C. (60·8° F.).
Barometer	29·6 inches.
Luminosity corrected to 120 grs. sperm, and 5 cubic feet hydrogen per hour	28·13 candles.
Ditto, and to 30 inches barometric pressure and 60° F.	28·58 „

Percentage of benzol vapour in gas 7·6; or 100 vols. of hydrogen passing meter, took up 8·22 vols. of benzol vapour.

* We find that ordinary sulphuric acid (SO_2HO_2), absorbs benzol-vapour rather rapidly, and may be used for its eudiometric determination.

B. *Benzolized Carbonic Oxide.*

The carbonic oxide was prepared by heating a mixture of potassic ferrocyanide and concentrated sulphuric acid, and was freed from traces of carbonic anhydride by passage through concentrated solution of caustic soda. The gas was then manipulated in the manner just described for hydrogen. It was, however, found impossible to burn carbonic oxide from a fish-tail burner, under suitable conditions, at a greater rate than 4·22 cubic feet per hour. The following results were obtained:—

Rate at which carbonic oxide passed through meter 4·22 cubic feet per hour.

Temperature of water in which benzolizer was immersed	13·0° C. (55·4° F.).
Temperature of room	15·0° C. (59·0° F.).
Barometer	28·88 inches.
Luminosity corrected to 120 grs. sperm, and 5 cubic feet of carbonic oxide per hour	22·66 candles.
Ditto, and to 30 inches barometric pressure and 60° F.	23·48 „

Percentage of benzol vapour in gas 6·0, or 100 vols. of carbonic oxide took up 6·38 vols. benzol vapour.

C. *Benzolized Marsh-gas.*

The marsh-gas used in these experiments was made by heating a mixture of sodic-acetate and soda-lime in an iron mercury bottle. So prepared it was far from pure, as the following results of its analysis show; but we were unable, by this process conducted upon a sufficiently large scale, to obtain a purer product, and we shrank from the labour necessary to prepare so large a quantity of pure marsh-gas from zinc-methyl. Indeed had we resorted to this latter method the diffusion of atmospheric air into the pure gas could scarcely have been prevented.

Composition of the crude Marsh-gas used in the experiments.

Marsh-gas	70·08
Hydrogen	20·60
C_nH_{2n}	·55
Nitrogen	8·17
Oxygen	·60
	100·00

Burnt at the rate of 5 cubic feet per hour this gas gave the light of 1·4 standard candle. After passing through the benzolizer it was found impossible to consume the gas from a fish-tail burner, under suitable conditions for the development of light, at a greater rate than 2·96 cubic feet per hour. The following numbers were recorded in two series of observations:—

	I.	II.
Rate at which marsh-gas passed through meter .	2·96 cub. ft. per hour	2·85 cub. ft. per hr.
Temperature of water in which benzolizer was immersed.....	13·0° C. (55·4° F.)	12·0° C. (53·6° F.)
Temperature of room....	25·0° C. (77·0° F.)	22·0° C. (71·6° F.)
Barometer	30·2 inches	30·4 inches
Luminosity corrected to 120 grains sperm, and 5 cubic feet marsh-gas per hour	29·75 candles	22·92 candles
Ditto, and to 30 inches bar. press. and 60° F..	30·56 „	23·10 „
Ditto, after deducting 1·4 candle for luminosity of C_nH_{2n} in marsh-gas	29·16 „	21·70 „
Percentage of benzol-vapour in gas.....	6·1	4·44
100 vols. of marsh-gas took up of benzol-vapour.....	6·49	4·66

The results of the foregoing experiments may be thus summarised:—

5 cubic feet of hydrogen after benzolization at 14·8° C., gave for one hour the light of	28·58 candles.
5 cubic feet of carbonic oxide after benzolization, at 13·0° C., gave for one hour the light of	23·48 „
5 cubic feet of marsh-gas after benzolization at 13·0°, gave for one hour the light of	29·16 „
5 cubic feet of marsh-gas, after benzolization at 12·0° C., gave for one hour the light of.....	21·70 „

But the volumes of benzol vapour taken up by 100 vols. of the three gases at the different temperatures just specified were:—

For hydrogen	8·22	vols. at	14·8° C.
„ carbonic oxide	6·38	„	13·0° C.
„ marsh-gas (1st experiment)	6·49	„	13·0° C.
„ „ (2nd „)	4·66	„	12·0° C.

Otherwise expressed it may be stated that, measured at 60° F. and 30 inches barometric pressure—

·410 cubic foot of benzol vapour burnt with H gave for one hour the light	28·58 candles.
·320 cubic foot of benzol vapour burnt with CO gave for one hour the light of	23·48 „
·3154 cubic foot of benzol vapour burnt with CH_4 gave for one hour the light of	29·16 „
·231 cubic foot of benzol vapour burnt with CH_4 gave for one hour the light of	21·70 „

Hence at the standard temperature and pressure—

1 cubic foot of benzol vapour burnt with H gave for one hour the light of	69·71 candles.
1 cubic foot of benzol vapour burnt with CO gave for one hour the light of	73·38 „
1 cubit foot of benzol vapour burnt with CH_4 gave for one hour the light of	92·45 „
1 cubic foot of benzol vapour burnt with CH_4 gave for one hour the light of	93·94 „

Or if

n cubic feet of benzol vapour burnt with H give for one hour the light of 1 candle, then

n cubic feet of benzol vapour burnt with CO will give for one hour the light of 1·053 candle;

n cubic feet of benzol vapour burnt with CH_4 will give for one hour the light of 1·326 candle;

n cubic feet of benzol vapour burnt with CH_4 will give for one hour the light of 1·347 candle.

Now 1 cubic foot of benzol vapour at 60° F. and 30 in. bar. press. weighs 1,444 grains, and therefore 1 lb. (7,000 grains) of benzol burnt with hydrogen gives a light equal to that of 337·9 sperm candles for one hour, or 5·793 lbs. of spermaceti.

Hence 1 lb. avoirdupois of benzol gives when burnt with—

H	the light yielded by	5·793	lbs. of spermaceti.
CO	„ „	6·100	„ „
CH_4	„ „	7·682	„ „
CH_4	„ „	7·803	„ „

The light evolved by the luminiferous constituents of coal gas is therefore not altogether independent of the proportion of the diluents (hydrogen, carbonic oxide, and marsh-gas) with which they are mixed; for the foregoing experiments show that a given weight of benzol produces 5·3 per cent. more light when it is diluted with carbonic oxide than when it is diffused in hydrogen, and between 32·6 and 34·7 per cent. more in marsh-gas than in hydrogen, and the last numbers would doubtless have been still higher had the marsh-gas been pure.

This difference in the luminosity of benzol when burnt in different media is probably due, in part at least, to the different pyrometric thermal effects of the three gaseous media employed.

The *actual* pyrometric effects of hydrogen, carbonic oxide, and marsh-gas when burnt in atmospheric air have never been determined, but *calculated* from their absolute thermal effects as measured by Favre and Silbermann, the temperatures of their flames would be—

Hydrogen.....	2,080° C.
Carbonic oxide	2,828°
Marsh-gas	1,935°

The *actual* pyrometric effects of hydrogen and marsh-gas are probably nearly equal, whilst that of carbonic oxide is considerably higher. Berthelot, however, estimates the average pyrometric effect of carbonic oxide burnt in air (1,975° C.) to be only 75° C. higher than that of hydrogen (1,900° C.). If the actual pyrometric effects of the three gases bear the same relation to each other as the calculated values, the greater amount of light emitted by benzol when burnt with carbonic oxide, receives a satisfactory explanation, but the still higher illuminating effect obtained by burning the benzol in marsh-gas is not accounted for. It has been shown by one of us (*Journal of Gas Lighting*, 1867) that marsh-gas burns with a flame of considerable luminosity when it is heated to about 300° C. along with the air necessary for its combustion, and it is certain that the pyrometric effect of marsh-gas would be augmented by the presence of 5 cr 6 per cent. of benzol vapour, but whether this is the sole cause of the increased light must be determined by further investigation.

XIV.—*Action of Reducing Agents on Potassium Permanganate.*

By Francis Jones, F.R.S.E.

In a paper on Stibine (this *Journal*, xxix, 642), read before this Society last year, I mentioned incidentally that this gas and its analogues decompose solution of potassium permanganate with separation of oxide of manganese. I also pointed out that the precipitate consisted only of oxide of manganese, and that the antimony, arsenic, &c., passed into solution.* I have since examined these reactions more fully, as well as the action of hydrogen itself, which has long been known to act on permanganates (*Gmelin's Handbook*, iv, 211). The results show that hydrogen, ammonia, phosphine, arsine, and stibine all decompose permanganates with separation of hydrated sesquioxide of manganese, and formation of salts of phosphorus, arsenic, &c.

The experiments were made by passing the purified gases into a moderately strong solution of potassium permanganate until the disappearance of the purple colour. The precipitate was then allowed to settle, washed by decantation, and dried over sulphuric acid or on the water-bath. The liquid was poured off, filtered, and examined qualitatively. The oxides were analysed in various ways, but generally by reduction in hydrogen to protoxide, or by ignition in air to manganoso-manganic oxide. Occasionally the combined water was also estimated as a check.

I. *Action of Hydrogen.*

(*a.*) *In Neutral Solutions.*—When hydrogen is passed through a neutral solution of potassium permanganate, a light brown precipitate soon separates, but settles very slowly. After the prolonged action of the gas the precipitate becomes denser, and the supernatant liquid becomes perfectly clear and colourless. This clear liquid is alkaline to test-paper, and contains only potash; the precipitate is hydrated sesquioxide of manganese. The reaction may be thus represented:—

$$2KMnO_4 + 8H = Mn_2O_3 + 2KHO + 3H_2O.$$

Analysis of Oxide.

	Substance.	MnO.	Per cent. Mn.	Calculated.
A.	0·4465 gram	0·3658 gram =	63·44	62·50 ($Mn_2O_3 + H_2O$)

* E. Schobig has since proposed this reaction as a means of purifying hydrogen from these gases, a method which I had likewise adopted with excellent results. *J. pr. Chem.* [2], xiv, 289.

The absorption of hydrogen by solution of permanganate is tolerably rapid, and increases with the temperature and with the surface of liquid exposed to the action of the gas. It may be shown experimentally, by filling a wide test-tube with hydrogen, and placing it mouth downwards in a solution of permanganate; the solution will steadily rise in the tube until all the hydrogen has been oxidised. Or, if a tube filled with hydrogen and containing a few drops of a saturated solution of permanganate be sealed up and shaken from time to time, the whole of the hydrogen will be oxidised in two or three days, so that, if the end be broken off under water, the liquid will rise to the top of the tube. A similar result may be obtained in half-an-hour by placing the sealed-up tube for that length of time in a water-bath.

(*b.*) *In Acid Solutions.*—The permanganate was acidified with a few drops of pure dilute sulphuric acid, and the hydrogen passed through. A precipitate soon separated, darker in colour than in the neutral solution, and very dense. It consisted of manganese sesquioxide; the filtrate contained only potassium sulphate.

Analyses of Oxide.

Substance.	MnO = per cent. manganese.		Calculated.	
B. 1·8040 gram	1·455 gram	= 62·50	62·50	$Mn_2O_3 + H_2O$
C. 0·4318 „	0·3408 „	= 61·14	62·50	
D. 0·6220 „	0·5395* „	= 62·49	62·50	

(*c.*) *In Alkaline Solutions.*—Pure caustic soda was added to the permanganate; the hydrogen acted much more slowly than in the previous cases; the liquid first became green, by reduction to manganate, and this colour disappeared only after the prolonged action of the gas. The precipitate was pale brown, and very similar in appearance to that produced in neutral solutions.

Analyses of Oxide.

Substance.	MnO = per cent. manganese.		Calculated.	
E. 0·5415 gram	0·4410 gram	= 63·08	62·50	$Mn_2O_3 + H_2O$
F. 0·5940 „	0·4850 „	= 63·24	62·50	

II. *Action of Ammonia.*

The action of ammonia on potassium permanganate has been examined by several chemists. It is stated to precipitate hydrated peroxide of manganese and to evolve nitrogen (*Gmelin's Handbook*, iv, 237). Wöhler (*Jahresbericht*, 1865, p. 150) found that nitrous acid was also produced in quantity.

* Weighed as Mn_3O_4.

On adding a strong solution of ammonia to one of permanganate, the mixture becomes hot, nitrogen is slowly evolved, and a brown flocculent precipitate of manganese sesquioxide separates out. The filtrate contained potassium nitrite and nitrate. The reaction may be represented by the following equation:—

$$8KMnO_4 + 8NH_3 = 4Mn_2O_3 + KNO_3 + KNO_2 + 6KHO + 9H_2O + 6N.$$

Analysis of Oxide.

Substance.	MnO	Calculated.	Water. Found.	Water. Calculated.
G. 1·0613 gram	0·1508 = 62·09	62·50	10·71	10·22

III. *Action of Phosphine.*

Phosphine, prepared by warming phosphorus with solution of potash, was passed through a series of flasks containing solution of potassium permanganate (the air had been previously expelled from the apparatus by a current of hydrogen). The escaping gas was not spontaneously inflammable so long as any permanganate remained undecomposed; the completion of the reaction was therefore easily noted by the gas regaining this property at the exit-tube of the apparatus. The excess of phosphine was expelled by hydrogen, and the precipitate collected and analysed. One portion of the oxide dried over sulphuric acid was found to contain a molecule more of water than the other portion, which was dried on the water-bath, but in each case the oxide obtained was the sesquioxide.

The filtrate was quite clear and colourless, and had a slightly alkaline reaction. It gave the reactions both of phosphorous and phosphoric acids. These changes may be thus represented:—

$$6KMnO_4 + 4PH_3 = 3Mn_2O_3 + 2K_2HPO_3 + 2KH_2PO_3 + 3H_2O$$

and $$2KMnO_4 + PH_3 = Mn_2O_3 + K_2HPO_4 + H_2O.$$

Analyses of Oxide.

Substance.	MnO = per cent. of manganese.	Calculated.	
H. 0·7804 gram	0·5674 gram = 56·31	56·70	($Mn_2O_3 + 2H_2O$)
I. 0·7995 „	0·6328 „ = 61·31	62·50	($Mn_2O_3 + H_2O$)

IV. *Action of Arsine.*

Arsine, prepared by allowing a solution of arsenic in hydrochloric acid to drop on granulated zinc, and purified by passing the gas through a dilute solution of soda, was passed into a neutral solution of potassium permanganate. The colour of this solution rapidly disappeared, and a dark brown precipitate, which contained a trace of arsenic, separated out. The precipitate was found on analysis to be

manganese sesquioxide; the filtrate, which was faintly alkaline, contained only potassium arsenate. The reaction may be thus represented*:—

$$2KMnO_4 + AsH_3 = Mn_2O_3 + K_2HAsO_4 + H_2O.$$

Analyses of Oxide.

	Substance.	MnO = per cent. manganese.		Calculated.
J.	0·8250 gram	0·6135 gram	= 57·60	56·70 ($Mn_2O_3 + 2H_2O$)
K.	1·0200 „	0·8325 „	= 63·19	62·50 ($Mn_2O_3 + H_2O$)

V. *Action of Stibine.*

This gas, prepared similarly to arsine, behaved like that gas, except that the precipitate was more flocculent; the filtrate contained potassium antimonate and a small trace of manganese. The reaction may be thus represented—

$$2KMnO_4 + SbH_3 = Mn_2O_3 + K_2HSbO_4 + H_2O.$$

Analyses.

	Substance.	MnO.		Per cent. Mn.	Calc.	Water. Found.	Water. Calc.
L.	0·9100	0·7465	=	63·53	62·50	9·81	10·22
M.	0·8895	0·7075	=	61·61	62·50	—	—

So far then, the results show that ammonia and its analogues react on potassium permanganate in a closely similar manner, and that hydrogen agrees with them in so far as the nature of the precipitated oxide is concerned; it is uniformly the hydrated sesquioxide. On extending the investigation to the action of other reducing agents on potassium permanganate, I obtained as before precipitation of the sesquioxide, but accompanied (in all the cases I have examined) by the *liberation of oxygen.* I now give these results.

VI. *Action of Oxalic Acid.*

The action of oxalic acid on permanganates has been made the subject of investigation by many chemists. Berthelot (*Jahresbericht*, 1867, page 334) found that it is oxidised to carbon dioxide and water, not only in acid, but also (though slowly) in alkaline solutions. Vernon Harcourt (this *Journal* [2], v, page 460) in a paper on the

* Schobig (*loc. cit.*) represents this reaction by the following equation, but gives no proof of the formation of the various products formulated—

$$10H_3As + 16KMnO_4 = 5K_3AsO_4 + KMnAsO_4 + 2Mn_3(AsO_4)_2 + 9Mn(OH)_2 + 6H_2O.$$

The reaction has also been studied recently by Parsons (*Chemical News*, 1877, page 236), who represents it by the following equation:—

$$3K_2Mn_2O_8 + 4AsH_3 = 3Mn_2O_2(OH)_2 + 2As_2O_3 + 6KHO.$$

GENERAL LIBRARY University of MICHIGAN

action of oxalic acid on permanganate, gives the following equation for the reaction—

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

I find, however, that this equation does not express all that occurs, since *oxygen* is evolved along with the carbon dioxide, both when sulphuric acid is present and when it is absent.

On adding solution of potassium permanganate to a warm solution of oxalic acid, the purple colour of the former rapidly disappears; the liquid remaining colourless up to a certain point, when oxalate of manganese separates out even in the warm liquid. Beyond this point, the further addition of permanganate produces a brownish coloration, and then precipitation of oxide of manganese, which continues until the whole of the oxalate has been decomposed. The reaction of the liquid, acid at first, changes to neutral, and finally to alkaline. Carbon dioxide is evolved from the beginning to the end of the oxidation, and along with it *oxygen*.

These two stages in the reaction may be represented by the following equations:—

(a.) $2KMnO_4 + 8C_2H_2O_4 = 2MnC_2O_4 + K_2C_2O_4 + 10CO_2 + 8H_2O,$
(b.) $2MnC_2O_4 + 2KMnO_4 = 2Mn_2O_3 + K_2CO_3 + 3CO_2 + O.$

The presence of oxygen in the evolved gases was ascertained by experiments made in one or other of the following ways:—

(1.) Solutions of oxalic acid and potassium permanganate were separately poured into a long glass tube which was completely filled, then closed with the thumb, inverted and opened under water contained in a small beaker. The liquids soon mixed by diffusion and bubbles of gas rose to the top of the tube. When no more gas was evolved, the quantity obtained was decanted into another tube, shaken up with caustic soda to remove the carbon dioxide, and the residual gas tested for oxygen in the usual way.

(2.) A flask was closed with an india-rubber stopper through which passed three glass tubes; one of these reached to the bottom of the flask, and was connected with an apparatus evolving carbon dioxide, another conveyed the evolved gases to a glass gas holder, and the third was wide enough to admit the point of a stoppered burette which was fitted air-tight into the tube. The flask contained the liquid to be examined (*e.g.*, oxalic acid solution or oxalic mixed with dilute sulphuric acid), the burette contained the permanganate. With this apparatus an experiment was made by first expelling the air with a current of carbon dioxide which was stopped as soon as the air was expelled. The permanganate was then allowed to flow in, and the gases produced by the reaction were received in the glass gas-holder

which contained solution of caustic soda to absorb the carbon dioxide. The unabsorbed gas was collected in a tube and tested for oxygen as before.

I intend to make this reaction of oxalic acid on permanganate the subject of further investigation, and in the meantime need only say that in whatever way I varied the conditions of the experiment, oxygen was uniformly obtained as a product of the reaction; so that, whether there be excess of oxalic acid or of permanganate, whether the solutions be strong or dilute, whether another acid be present or not, in each case oxygen is evolved.

It could scarcely be doubted that other reducing agents than oxalic acid might act similarly on permanganate, and liberate oxygen. I therefore examined its action on ferrous salts, and at once perceived that this was the case; oxygen is evolved in presence or absence of acids, in dilute or in strong solutions. Further, a few experiments soon showed me, that in the action of sulphuric acid upon manganese dioxide in presence of an oxalate, oxygen is evolved along with the carbon dioxide. Obviously, these observations are of importance in connection with the analysis of manganese dioxide, and with the use of permanganate in volumetric analysis.

VII. *Manganese Chloride.*

When a strong solution of permanganate is added to one of manganese chloride, sesquioxide of manganese separates out and bubbles of gas are evolved. On examining this gas I found it to consist of a mixture of chlorine and oxygen. The reaction may be thus represented—

$$MnCl_2 + KMnO_4 = Mn_2O_3 + KCl + Cl + O.$$

On mixing dilute solutions of the same salts, oxygen was evolved, but not chlorine. I also ascertained that oxygen is evolved when manganese sulphate is added to solution of potassium permanganate.

Analysis of Oxide.

Substance.	MnO = per cent. of manganese.	Calculated.	
N. 0·879 gram	0·705 gram = 62·13	62·50	($Mn_2O_3 + H_2O$)

It will be noticed in the preceding experiments that the oxide of manganese uniformly precipitated is the sesquioxide, and *not* the dioxide, which is generally stated to result from the decomposition of permanganates.

If the dioxide be actually precipitated, I think it not improbable that it at once decomposes into sesquioxide and oxygen (hence the oxygen in the above experiments), behaving in this respect like manganese tetrachloride, which is formed when cold hydrochloric acts

upon manganese dioxide, but which soon splits up into the dichloride and free chlorine. And if the dioxide be not obtained by the reduction of permanganates, it seemed doubtful whether it can be obtained at all by precipitation.

Some confirmation of this supposition was obtained by an examination of two oxides prepared by methods which are said to yield the hydrated dioxide of manganese, viz., the oxide obtained by the addition of bromine to a mixture of a manganese salt with ammonia, and the oxide obtained in Weldon's process for the recovery of manganese from the chloride.

In the former case the oxide contained 62·36 per cent. of manganese, in the latter the oxide, after washing with dilute nitric acid to remove lime, &c., was found to contain 62·57 per cent. of manganese. Both these analyses agree closely with the formula, $Mn_2O_3 + H_2O$, which requires 62·50 per cent. of manganese.

Summary.

(*a.*) Hydrogen decomposes neutral, alkaline and acid solutions of potassium permanganate, with separation of sesquioxide of manganese in each case.

(*b.*) Hydrogen left in contact with solution of permanganates is completely absorbed at the ordinary temperature, more rapidly at 100° C.

(*c.*) Ammonia decomposes potassium permanganate with liberation of nitrogen, separation of manganese sesquioxide, and formation of potassium nitrite and nitrate.

(*d.*) Phosphine precipitates sesquioxide, and potassium phosphite and phosphate are formed.

(*e.*) Arsine precipitates sesquioxide, and potassium arsenate is formed.

(*f.*) Stibine precipitates sesquioxide, and potassium antimonate is formed.

(*g.*) The first action of oxalic acid on potassium permanganate results in the formation of manganese and potassium oxalates, water and carbon dioxide. After this stage has been reached, the further addition of permanganate produces precipitation of manganese sesquioxide, formation of potassium carbonate, and evolution of carbon dioxide and oxygen. Oxygen is also evolved in presence of sulphuric acid.

(*h.*) Oxygen is evolved along with carbon dioxide when sulphuric acid acts on manganese dioxide in presence of an oxalate.

(*i.*) Oxygen is evolved when ferrous sulphate, manganese sulphate, or manganese chloride act on potassium permanganate.

XV.—*On the Decomposition-products of Quinine.*

By W. Ramsay, Ph.D., Tutorial Assistant of Chemistry, Glasgow University; and J. J. Dobbie, M.A., Clark Scholar in Nat. Sc., Glasgow University.

First Paper (Oxidation with Permanganate).

Cloez and Guignet (*Compt. rend.*, xlvii, 710), by oxidising quinine with permanganate of potash, obtained nitrate and carbonate of potassium and a *peculiar acid.*

With the view of examining this acid and the other products of decomposition of quinine, we repeated their experiment.

The oxidation, and subsequent separation of the acid were conducted in the following manner:—5 grams of quinine were treated with 50 grams of permanganate, at the ordinary temperature, a gentle heat only being applied to start the action. When reduction of the permanganate was complete, the alkaline liquid was filtered from the manganese dioxide and neutralised with nitric acid. On adding nitrate of lead to the hot neutral solution, a curdy white precipitate of the lead salt of the unknown acid was obtained. This salt was decomposed with a current of sulphuretted hydrogen, the liberated acid filtered from the lead sulphide, and evaporated to dryness. On taking up the residue with alcohol, the alcoholic solution deposited on standing a red powdery substance. The free acid, filtered from the red powder, was thrown down with silver nitrate, and the silver salt treated in the same way as the lead salt with sulphuretted hydrogen. The filtrate from the silver sulphide, on being slowly evaporated over sulphuric acid, gave delicate needle-like crystals of the free acid. A small portion of the acid thus liberated, on being heated, gave off the smell characteristic of the decomposition by heat of *dicarbopyridenic acid*, and afforded strong evidence in favour of the identity of the acid produced from quinine with that which Professor Dewar obtained by oxidising picoline with potassium permanganate.

The acid from quinine has been obtained in two different forms—viz., in plates and in short prisms. As yet we have not succeeded in getting the long hair-like needles, in which dicarbopyridenic acid crystallises when free from water.

On heating for several hours at 100°C., 0·3373 gram of the acid lost 0·0324 gram = 9·6 per cent.

$C_7H_5NO_4.H_2O$ contains 9·83 per cent. H_2O.

Combustion of 0·1334 gram acid gave 0·338 gram H_2O, and 0·218 gram CO_2 = 3·16 per cent. H, and 44·56 per cent. C.

Dicarbopyridenic acid contains H, 3·00 per cent.; C, 50·30 per cent. The carbon of the acid obtained from quinine is thus between 5 and 6 per cent. lower than that of dicarbopyridenic acid; but as the quantity burned was very small and apparently not quite pure, the approximation of the results obtained by experiment to the calculated percentage of C and H in dicarbopyridenic acid may, taken together with the facts to be mentioned, render the identity of the acids at least highly probable. A qualitative examination of the acid showed that it contained nitrogen.

Owing to the difficulty of getting entirely rid of the red powder already mentioned—a trace of which always comes down with the salts—it was found impossible to make an exact determination of the melting point. The purest specimen obtained blackened below 200°, and melted apparently at 251—252°. The melting point of dicarbopyridenic acid is 237·5°; but this can be observed only when very pure specimens are used. With ferrous sulphate the acid gave the red colour characteristic of dicarbopyridenic acid.

The silver salt of the acid comes down in boiling solution as a white curdy precipitate. 0·1425 gram of the salt gave 0·0801 gram Ag = 56·21 per cent. The neutral silver salt of dicarbopyridenic acid contains 56·69 per cent. Ag.

The silver salt, on heating, behaves like mercury sulphocyanide. The silver salt of dicarbopyridenic acid has the same peculiarity.

On titrating the acid with a standard solution of potash, 0·2948 gram acid required for neutralization 0·1692 gram K_2O = 0·1404 gram K. Calculating this amount of potassium to hydrogen, we obtain 0·00358 gram, as the weight of hydrogen replaced by potassium; therefore, 0·2948 gram less 0·00358 gram, plus 0·1404 gram = 0·43162 gram = the amount of potassium salt formed, and $\frac{100 \times 0{\cdot}1404}{0{\cdot}43162}$ = 32·50 per cent.

The percentage amount of potassium in the neutral potassium salt is therefore 32·50.

The corresponding salt of dicarbopyridenic acid contains 32·15 per cent. K.

On titrating the acid from the products of another oxidation with soda in the same way, 0·0792 gram acid required for neutralization 0·0239 gram Na_2O = 0·0218 gram Na. Calculating this to H as before, we find 0·00095 gram. Therefore, 0·0792 gram, less 0·00095 gram, plus 0·0218 gram = weight of salt = 0·10015 gram, and $\frac{100 \times 0{\cdot}0218}{0{\cdot}10015}$ = 21·76 per cent. Percentage of Na in salt = 21·76.

The neutral sodium salt of dicarbopyridenic acid contains 21·80 per cent. Na.

These results—the analysis of the silver and alkali salts, the analysis of the acid itself and its behaviour on burning, and with ferrous sulphate—seem to leave but little doubt as to the identity of the acid which we have obtained from quinine with that got in the same way from picoline.

Unfortunately the very high price of quinine prevented us in the first instance working with a quantity sufficient to give a yield of the acid large enough for a complete investigation. Having ascertained how the acid may be most economically separated, it was our intention to repeat our experiments on a larger scale; but as the attention of others (*Deut. Chem. Ges. Ber.*, 1877, p. 1930) has recently been directed to the same acid, we believe that it is unnecessary to apologize for the immediate publication of our results in their present imperfect form.

It has been mentioned, that on dissolving in alcohol the residue obtained by evaporation of the filtrate from the lead salt, the solution, after standing for some time, gave a red deposit. This red substance is probably a product of imperfect oxidation, and seems to be identical with Marchand's quinetin, which is obtained by oxidizing quinine with peroxide of lead and sulphuric acid. If the oxidation of quinine with potassium permanganate, instead of being conducted at the ordinary temperature, is carried on at 100° C., the quantity of red substance obtained is less, and the yield of acid greater.

M. Marchand having kindly furnished us with the details of his method of oxidation with peroxide of lead, we prepared a quantity of quinetin. On subjecting this quinetin to oxidation with permanganate, we obtained an acid apparently identical with that got by the direct oxidation of quinine.

At present we are engaged in investigating the nature of Marchand's quinetin, and in our next paper shall give the results of that investigation, together with those of experiments on the action of barium hydrate, and various oxidising agents on quinine and allied alkaloids.

XVI.—*On the Estimation of Phosphorus in Iron and Steel.*

By Edward Riley.

The accurate determination of the amount of phosphorus present in iron and steel, more especially since the introduction of the Bessemer and Siemens-Martin processes, now so largely used, has become of the greatest technical importance.

The method most generally employed at iron and steel works is

that known as the molybdate method, the other is known as the magnesia method; the latter is not so much used, as the results cannot be obtained so quickly. I need hardly say that in iron and steel works, where so many determinations are required, time is a most important consideration.

It is not my intention, in this communication, to enter into very minute details as to the method employed in precipitating phosphorus by molybdic acid, or by molybdate of ammonia; as it has been so frequently described in various works, and I find practically that almost every operator varies in the exact method he employs.

The percentage of phosphorus is as a rule so small in the pig iron used and the steel made, that to determine it accurately requires much practice and some amount of analytical skill.

Speaking from my own experience of more than 25 years, and from my experience and observation as to the results obtained by others who use the molybdate method, I must say that as a practical fact the results obtained by many chemists by it are not satisfactory.

I have hesitated to adopt it in my laboratory, although I must admit I have on some occasions obtained very satisfactory results; still I have always felt a certain amount of doubt about the process, whereas with the magnesia method I have no doubt whatever. I must however admit that grave errors may be made by the magnesia method, and that great care is required in using it.

It is quite the exception to find either iron or steel without phosphorus, only some very few Swedish and foreign irons are free from it. I have, however, very frequently samples and analyses sent to me in which no phosphorus is given, whereas on examining the samples I find in most cases a very appreciable and weighable amount. I am speaking now of analyses made by chemists who have some experience in iron and steel analysis; by others it is not at all unfrequent for ·10 to ·20 per cent. to be overlooked.

The cause of this low estimation, or failing to detect the phosphorus, is, I believe, in the case of the molybdate method, due to having the solution too acid, or in other cases not adding a sufficient amount of molybdate solution. In the case of high estimates, which are not unfrequent, the excess is due to molybdic acid being thrown down together with the phosphorus precipitate.

The great importance of the accurate determination of phosphorus, induced me to have a series of experiments made by various operators, so as to ascertain how nearly the practical results obtained in iron and steel works, and in various metallurgical laboratories, actually agreed with the absolute amount of phosphorus present.

For this purpose pure peroxide of iron was prepared, ordinary iron borings were dissolved in dilute sulphuric acid, the solution filtered

University of Michigan

from the residue, and the sulphate of iron crystallised out; the mother-liquor was separated and the crystals washed with distilled water, re-dissolved in distilled water and recrystallised. The crystals having again been washed, were then dissolved in distilled water, the solution peroxidised with pure nitric acid, and the peroxide of iron precipitated from the diluted solution with ammonia. After washing four times by decantation, the precipitate was redissolved in pure hydrochloric acid, and reprecipitated by ammonia; the oxide of iron was washed until it was practically free from ammoniacal salts, then detached from the calico filter used, dried and ignited at a dull red heat in a muffle.

Before using the peroxide it was thought desirable to ascertain if it was absolutely free from phosphorus. It was tested by the magnesia method usually employed by me.

The peroxide of iron was dissolved in strong hydrochloric acid, then reduced, after diluting the solution with sodium sulphite, and the excess of sulphurous acid was expelled by boiling; the solution was nearly neutralised with ammonia, acetate of ammonia added; the phosphoric acid was then precipitated on boiling with a small amount of peroxide of iron, as basic acetate and phosphate. When only minute quantities of phosphorus are present, there is usually enough peroxide of iron in the solution to precipitate the phosphorus; if not, a drop or two of a dilute solution of perchloride of iron is added, or a few drops of bromine-water, enough to make the precipitate of a red tinge.

The solution after boiling is filtered, the precipitate dissolved in strong hydrochloric acid (it is not necessary to wash the precipitate before dissolving it), and the filter thoroughly washed.

The solution of the phosphoric acid with some iron is then evaporated to a small bulk, about half an ounce (15 c.c.); to this is added about 200 grams of citric acid (13 grms.); the solution neutralised with ·960 ammonia; some 20 to 30 drops of magnesia solution added, then a moderate amount of ·880 ammonia, so as to make it strongly alkaline. The whole bulk of liquid should not exceed 1½ to 2 ounces (50 c.c.). No immediate precipitate is formed unless the phosphorus amounts to ·10 or more per cent.; on standing, however, for a night, the characteristic small star-shaped crystals of the ammonia-magnesium phosphate are found adhering to the sides of the beaker and on the stirrer. The solution is strongly agitated the next day with the stirrer, either at once or after the lapse of a little time, whereupon a further precipitate of the granular characteristic ammonia phosphate is formed. The solution is allowed to stand for another night, and filtered off on the following day; and the residue is washed with ammonia-water, dried, ignited, and weighed.

The precipitate, after ignition, is either perfectly white or coloured

only with a little carbon. If any difficulty is experienced in burning this over the gas, it may be heated with a few drops of fuming nitric acid with the cover over the crucible; it then becomes perfectly white. In no case do I find that any iron is precipitated with the magnesia salt.

The precautions necessary are to have not too much iron present. I have found that the usual quantity is from 5 to 6 grains of iron from a phosphorus determination on 150 grains of steel. A large excess of citric acid must be used, and also of ammonia. The solutions should be of a paleish yellow-green colour; if it is very distinctly red, good results are not obtained; if it is dark-red, the results are altogether fallacious.

The precipitate obtained by magnesia is so characteristic that there cannot possibly be any mistake about it.

The peroxide of iron was found to contain a distinct amount of phosphorus; 206·595 grains gave $Mg_2P_2O_7$·0135 grain.

Equal to phosphorus per cent. in the Fe_2O_3	·0018.
„ „ in iron or steel	·0026.

Some pure $Mg_2P_2O_7$ was prepared by taking about ½-pint of magnesia solution, made by adding a considerable amount of ammonia and chloride of ammonium to a saturated solution of ordinary sulphate of magnesia, and filtering off the precipitate and insoluble matter; this solution on standing generally yields a deposit. The clear solution is used for phosphorus determinations.

To the above solution, after dilution, was added phosphate of soda, the precipitate formed was allowed to settle, the supernatant liquid decanted off; and the precipitate washed four times with distilled water; it was then redissolved in hydrochloric acid, reprecipitated with ammonia, filtered, and washed until no appreciable residue was left on evaporating the washings to dryness.

The dried precipitate was ignited in a muffle until it was quite white.

In carrying out the experiments, each of my assistants ignited from 213 grams to 218 grams of the pure peroxide of iron, this quantity representing about 150 grams of metallic iron, the usual quantity taken for phosphorus determinations in steel.

The above quantity was dissolved in strong hydrochloric acid. I then very carefully myself weighed out the phosphorus salt, giving each a different quantity. The solution of the peroxide was poured on the magnesium phosphate in a small beaker, and warmed until it was completely dissolved.

The phosphorus was then determined by my ordinary method, each

assistant working on a solution of iron containing a quantity of phosphorus unknown to him.

The following are the results that were obtained by each:—

		Peroxide of iron taken.	$Mg_2P_2O_7$ added.	$Mg_2P_2O_7$ found.	$Mg_2P_2O_7$ reprecipitated.
I.	W. H. Herdsman	218·62	·46	·475	·460
II.	A. E. Tucker	213·45	·48	·500	·500
III.	G. A. Jarvis	215·26	·35	·380	·365
IV.	F. J. Bolt	214·255	·72	·775	·745
V.	A. L. Hughes	215·215	·71	·725	—

Converting the peroxide of iron into metallic iron, and calculating the percentage of phosphorus present in the iron (after deducting the small amount of phosphorus found in the peroxide), the results are as follows:—

	Peroxide of iron to metallic iron.	Phosphorus p. c. added.	Phosphorus p. c. found.	Difference p. c. in phosphorus.
I.	153·034	·0839	·0840	·0001
II.	149·415	·0897	·0908	·0011
III.	150·682	·0648	·0678	·0030
IV.	149·978	·1340	·1417	·0077
V.	150·650	·1316	·1336	·0020

or a mean error in excess of ·0028 per cent.

In all cases the calculation is made on the first precipitation and weighing of the magnesium phosphate.

The first four, as my assistants, have had considerable practice in determining phosphorus. No. 5 determination was made by one of my pupils who has had but little practice, not having made more than three or four determinations of phosphorus in iron and steel. The above were the only experiments made, and it will be seen that practically the exact amount of phosphorus was obtained that I weighed in.

In reprecipitating the $Mg_2P_2O_7$ after weighing, it was dissolved in strong hydrochloric acid, a very small crystal of citric acid added, and excess of ammonia; and the precipitate after standing for two nights was filtered and weighed as before.

An experiment was made on some of the phosphate of magnesia to see what was the actual loss on reprecipitation.

$Mg_2P_2O_7$.	Ignited over Bunsen burner.	Ignited in muffle.
2·46 gave	2·445*	2·42

The experiment was made with the same bulk of liquid as in an ordinary phosphorus determination, and in precisely the same way, except that no citric acid or magnesia salt was added.

* Not quite white.

I should perhaps mention that when there is much phosphorus present, as in ordinary pig iron (not Bessemer pig), I operate on smaller quantities, and if there is much precipitate I use a rather larger bulk of liquid.

From the above experiment, and also from the results obtained in the previous experiments, it will be seen, as I have always found it, that there is no appreciable loss on reprecipitating the $Mg_2P_2O_7$, thus proving the practical purity of the precipitate obtained on the first precipitation.

In order to compare the results obtained by the molybdate method, 1,000 grains of the Fe_2O_3, weighed after ignition, were dissolved in hydrochloric acid; and to this 2·496 grams of ignited $Mg_2P_2O_7$ were added; after solution the whole was reprecipitated by ammonia, washed with distilled water, dried, ignited, and weighed.

The above quantity of magnesia salt represents in the iron calculated from the Fe_2O_3—

Phosphorus per cent.	·0994
Phosphorus in iron	·0026
	·1020

This gives the actual quantity of phosphorus present. To be quite certain that no mistake was made, Mr. Herdsman determined the phosphorus by the magnesia method.

Grams of Fe_2O_3.		$Mg_2P_2O_7$.		Phosphorus per cent. in iron.
213·27	gave	·52	equal	·0972
	or difference	—		·0048

Various portions, from 80 to 150 grains, were sent to three of the largest steel works in the country, where phosphorus determinations are made daily, by some of our most expert analysts of iron and steel; two other portions were sent, one to a well known chemist with a very large experience in iron and steel analysis, and another to a chemist also with a large experience, but not so well known.

The following are the results returned:—

Phosphorus per cent. by Molybdate Method.

I.	Phosphorus per cent.	·0780	
II.	„ „	·0749 ·0821	Mean, ·0785
III.	„ „	·0640	II. ..·0460
IV.	„ „	·0700	
V.	„ „	·0760	

Not taking into consideration the second result of No. III, which is obviously low, the mean of the five results is—

Phosphorus per cent.	·0733
Error in determinations per cent.	·0287

All the results are very concordant, except perhaps No. III, and all low, thus showing that phosphorus determinations as now carried out by our best operators are too low.

The above experiments were partly undertaken in consequence of a statement that my determinations of phosphorus in a steel rail were too high, and also that my results were always higher than those given by the Sheffield Steel Works.

Take the rail in question: the phosphorus was determined three times.

A.	150	grains of steel	gave	phosphorus	per cent.	·094
B.	200	,,	,,	,,	,, ...	·090
C.	150	,,	,,	,,	,, ...	·096

All the analyses were made by different operators.

The molybdate gave, analyses made at Steel Works—

A.	Phosphorus per cent.	·0602, ·0586 } ·0597
B.	,, ,, ...	·0976
C.	,, ,, ...	·076, ·086 } ·081

Mean by magnesia method.	Mean by molybdate.	Difference.
·0933	·0722	·0211

thus showing a difference between the results very closely approximating the difference in the previous case.

Take another case of same sample bars of steel.

Two of my assistants (one now at a steel works) made—

		I.	II.
		Magnesia method.	
A	Phosphorus per cent.	·172	·180
B	,, ,, ...	·162	·164
B′	Repeated by same operator.....	·165	·170
		Molybdate method.	
C	Chemist at Sheffield Steel Works returned	·267	·273

This high result differing so much from the above, the analyses were repeated, and the following results sent by same chemist:—

		Molybdate method.	
C′	Phosphorus per cent.	·142	·166
C″	,, ,, ...	·154	·154
D	Another ironworks chemist	·145	·158

thus clearly showing that the magnesia results are always higher.

I have had a very lengthy correspondence with chemists who have had considerable experience in the determination of phosphorus, mostly with chemists at iron and steel works. The opinion of several is that the two methods may be made to give the same results. This I think is quite possible, as the magnesia process may readily be worked to give slightly lower results.

In the case of the molybdate method, I find frequently that duplicate analyses are made on the same quantity of steel. Now it is quite possible that corresponding results may be obtained, and that they may be quite wrong, as I regard this as no check on an analysis. The better way is to take twice the quantity in one case to that taken in the other.

Before instituting the above experiments, I have most thoroughly tested the magnesia method, and had every confidence in its accuracy when carefully performed. I have used five times as much steel in one case as another, and obtained corresponding results, and numerous cases double, treble, and so on.

The experiments given, made by so many different operators, clearly shew, I think, that as the molybdate process is now carried out, the results are too low.

The method is, however, much more rapid than the magnesia process, and from experiments I have made, I think the molybdate process may be improved.

The method I propose is to dissolve the steel or iron in 1·20 nitric acid, avoiding as much excess as possible; to the solution, diluted to rather more than half a pint, sodium sulphite is added, so as to reduce the iron to FeO after boiling off the sulphite (a large excess should be avoided); the phosphorus is precipitated with some peroxide as basic acetate and phosphate, precisely as in the magnesia method; the precipitate is dissolved in hydrochloric acid; the solution made alkaline with ammonia; and the precipitate formed dissolved in 1·40 nitric acid. The solution is then precipitated with molybdate of ammonia in the ordinary way.

In an experiment made by Mr. Herdsman it was found that the phospho-molybdate came down at once; in twenty minutes the precipitate had settled; and in less than an hour after adding the molybdate, the liquid was filtered, and the precipitate ready to dry. The result obtained was phosphorus ·077 per cent. in a steel rail containing by the magnesia method ·093; it was found that some further precipitate of phospho-molybdate was formed on heating the filtrate.

Although this experiment was not successful, still I am inclined to think that by allowing a little more time, and with more practice, it may be made to succeed, and to give results more accurate than the

ordinary process, and in about the same time. I propose carrying out a series of experiments in this direction.

I have made no remarks on the method adopted by some chemists of dissolving the molybdate precipitate in ammonia and precipitating the phosphorus by a magnesia salt; this, in my opinion, is no improvement on the ordinary magnesia method (in iron or steel analyses).

In submitting the above results to the Society, I am under great obligations to the chemists who so readily assisted me in making the various phosphorus determinations, and also to the aid I have received from my assistants, more especially by my senior assistant, Mr. Herdsman, who has in fact carried out the larger number of analyses I have given.

XVII. *The Action of Sulphuric Acid on Copper.*

By Spencer Pickering.

Brackenbury Scholar of Balliol College, Oxford.

§ I. Although Maumené in 1846 made many analyses of the black substance which is generally formed during the action of sulphuric acid on copper, no one up to the present time has made a thorough investigation of the subject: it was, therefore, with a view to throw some light on the nature of this reaction, by studying the primary and ultimate products, and the circumstances which influence their formation, that the experiments detailed below were performed.

§ II. *Nature of the Reaction.*

There appear to be two, and only two, primary reactions, the one resulting in the formation of copper sulphate, sulphur dioxide and water, according to the following equation:—

$$1.\ Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O,$$

a reaction which may be regarded as consisting of two stages, the first being the formation of copper sulphate and nascent hydrogen, thus—

$$(a.)\ Cu + H_2SO_4 = CuSO_4 + 2H,$$

the second being the immediate action of the nascent hydrogen on another portion of the acid, forming sulphur dioxide and water, thus—

$$(b.)\ 2H + H_2SO_4 = SO_2 + 2H_2O.$$

The other primary reaction is expressed by the equation—

$$2.\ 5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O,$$

and this reaction, unlike the former one, does not necessitate the previous formation of nascent hydrogen. Of these two reactions either may take place alone or they may both occur together, and in various proportions. The other products which are found in the residue insoluble in water, and which are not accounted for by these equations, are the results of the decomposition of the subsulphide by the hydrogen sulphate, thus :—

$$Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + 2H_2O$$
$$CuS + 2H_2SO_4 = S + CuSO_4 + SO_2 + 2H_2O.$$

It was found that this residue invariably consisted of copper and sulphur only, and never contained oxygen, as stated by Berzelius and Maumené (comp. p. 135).

§ III. *Mode of Experimenting.*

The experiments were performed in a small flask of about 100 c.c. capacity, the gas liberated being passed through a short wide delivery tube into an ammoniacal solution of silver nitrate as a means of ascertaining whether any hydrogen sulphide was liberated or not: the temperature of the flask being kept constant by means of a water or oil bath. The acid employed was pure and strong—density 1·843—and it was always raised to the required temperature before the introduction of the copper, which latter was pure electrotype foil, 0·15 mm. in thickness, 3 grams exposing in all a surface of 65 square cm. The proportion of the metal and acid employed was 1 part of copper to 10 parts of hydrogen sulphate by weight; the actual quantities generally used being 3 grams of copper to 16·3 c.c. of acid. The time allowed in the majority of cases was 30 minutes. For the sake of obtaining more strictly comparable results, in many instances the same piece of copper was used in several experiments, due allowance being made for the relative increase of surface thus exposed; and for the same reason wherever possible, the temperature chosen was 100° C.; this temperature being more easily maintained constant than higher or lower ones.

§ IV. *General Appearance of the Action.*

Sulphuric acid attacks copper at all temperatures from 19° C. (and probably even still lower) upwards, to an extent increasing rapidly with the increase of temperature; with the exception of a few minute and occasional bubbles of sulphur dioxide no gas is evolved from the

liquid till about 130°: as soon as the copper begins to be attacked, its surface becomes dull and covered with a film of black subsulphide; when the amount of subsulphide floating in the liquid is small it exhibits a brownish colour, similar to that exhibited by small quantities of the protosulphide when suspended in a liquid; but as the quantity of subsulphide increases, the colour deepens and soon appears perfectly black. If the temperature be allowed to rise, the liquid generally begins to boil below 300° C., the boiling point of pure strong hydrogen sulphate being 327°; when the source of heat is withdrawn, the suspended sulphide subsides, leaving a bluish-green solution containing copper sulphate, which, on cooling, crystallises out from the acid in white acicular anhydrous crystals, leaving the hydrogen sulphate free from dissolved copper, and, when the proportion of metal and acid above mentioned is used, but little diminished in density. After the copper is entirely dissolved, and sometimes even before this, a deposit of sulphur appears in the neck of the flask.

On leading the gas evolved through water, collecting that portion of it which remains undissolved (the remainder being, of course, the air contained originally in the flask, &c.), and analysing it, it was proved that no gas insoluble in water, such as oxygen or hydrogen, was given off from the liquid during the action.

A small black precipitate deposited in the silver nitrate solution was at first mistaken for silver sulphide precipitated by evolved hydrogen sulphide, but this was afterwards found to be reduced silver sulphite, which latter is precipitated as soon as the ammonia becomes neutralised by the sulphur dioxide, and it was proved beyond doubt that in no case was any hydrogen sulphide liberated.

(*a.*) By replacing the test tube containing the silver nitrate by another similar tube with a fresh solution whenever the white silver sulphite made its appearance in the previous tube, and

(*b.*) By placing a roll of filter paper moistened with a solution of lead acetate in the delivery tube itself, and which never became darkened by the formation of any lead sulphide.

The copper sulphide appears to be deposited on the metal itself, and not in the liquid, the coating thus formed on the copper being compact, and, when the metal used is impure, difficult to remove. The sulphide shows no crystalline structure, but is quite amorphous. In determining its amount, it was transferred as quickly as possible by washing and other means to a weighed filter, and then carefully dried at 100° C.; after treating it with carbon disulphide to ascertain the presence, and if present, the amount of free sulphur which it contained, the whole or a portion of it was oxidised by hydrogen nitrate, the copper being generally determined by reduction with pure zinc, or else by Parke's potassium cyanide method, or as oxide by precipitation

with potassium hydrate; and the sulphur, partially in the free state, and partially as barium sulphate. (From the fact that in all cases where free sulphur was present and estimated as above, the sulphide left contained the amount of copper theoretically present in the protosulphide, I conclude that the sulphur was entirely soluble in carbon disulphide.)

Maumené mentions that the sulphide obtained in this way is "très altérable à l'air," and consequently in washing and drying it used many precautions which I found to be quite unnecessary. This subsulphide is not oxidised to the smallest appreciable extent either by washing with water not freed from air, or by exposure to air for a considerable time when moist or dry, or by drying in a steam bath at 100° C.; though in some cases it was dried over sulphuric acid *in vacuo*, then washed and dried again at 100° in air to ascertain whether any increase or diminution in weight was occasioned by employing this latter method, but none was found to have occurred. The protosulphide though more oxidisable than the subsulphide, is not too unstable to admit of being accurately estimated and analysed in the same way as the subsulphide; and when formed by the decomposition of this latter, as in the action of sulphuric acid on copper, it is more stable than when precipitated from a solution of a copper salt by hydrogen sulphide. Weighed portions of the subsulphide and of the protosulphide obtained in various experiments, and of the persulphide precipitated by hydrogen sulphide, were each exposed moist on filters for 14 days, after which—

None of the subsulphide had been oxidised.

1·8 per cent. of the protosulphide (from experiments) had been oxidised.

9·5 per cent. of the protosulphide (precipitated by H_2S) had been oxidised.

Again, some of the subsulphide which had been kept in a small bottle for several months, on being washed did not yield sufficient copper sulphate to give the slightest trace of colour when tested by potassium ferrocyanide, although some precipitated copper protosulphide which had been kept for the same length of time in a similar bottle showed that 43 per cent. of it had been oxidised. Many other experiments on the oxidisability of the different sulphides gave similar evidence.*

* That copper protosulphide varies in the facility with which it is oxidised, according to the method by which it is prepared, has been shown by Rose, who found that when this body is precipitated from solutions containing copper by ammonium sulphide, it is more oxidisable than when precipitated by hydrogen sulphide. It is generally stated that copper protosulphide is green, owing to the presence of copper sulphate, but this was shown to be incorrect by preparing some copper protosulphide, washing it with solution of hydrogen sulphide, and drying it

§ V. *Influence of Temperature.*

After a number of preliminary experiments, a series was made at constant temperatures ranging from 100° to 220° C.; the time allowed for each being 30 minutes. It was, however, soon apparent that those performed at the temperatures 170°, 195°, 220° C., in which cases the insoluble residue did not consist of copper subsulphide, were not comparable with the others, because at these higher temperatures the copper had entirely dissolved before the time allowed had expired, and consequently, secondary reactions might have taken place. The last experiments were therefore repeated, diminishing the time of action, so that in each case some of the copper taken might be left undissolved, and the results thus obtained, together with other experiments performed at lower temperatures, are given in Table I.

It will be seen on examining experiments 3 to 9 in this table, each of which is the mean of a great number, that the amount of copper dissolved in equal times (given for one minute in the last column) increases rapidly with the temperature, and also that the proportion of copper converted into sulphide to that converted into sulphate diminishes as the temperature is higher, till finally, at 270° C., we get no sulphide at all formed, the action consisting solely of the first of the primary actions given on page 112, namely—

$$1.\ Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

It will be seen on examining the second primary action—

$$2.\ 5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O,$$

that in this the proportion which the copper converted into sulphide bears to that converted into sulphate is two atoms to three atoms, and that this is the greatest proportion which could be formed if these two reactions are correct; and also, as will be shown below, the greatest ratio which could exist, according to any theory, of the formation of the sulphide. After performing experiments at temperatures from 100° upwards, and thus ascertaining that the proportion of sulphide

in a current of that gas, when it was proved to be green in colour, though no sulphate could possibly have been present in it. The protosulphide when obtained in the copper action is rather darker in colour than when precipitated by hydrogen sulphide; probably owing to the fact that the former is in a more compact state than the latter.

It is also stated that copper protosulphide is not attacked by cold hydrogen nitrate, and that the subsulphide is converted into the protosulphide; but this latter is undoubtedly attacked to a considerable extent, when *dry*, by cold hydrogen nitrate, and therefore also the subsulphide is, in all probability, not converted into the protosulphide by the action of this acid, but both sulphides are attacked to varying and indefinite extents.

to sulphate increased as the temperature was lower, it was thought probable that at still lower temperatures the proportion of 2 : 3 might be reached, *i.e.*, that the action (§ I, p. 112) might be obtained alone; and although in most cases, owing to circumstances not entirely evident, this ratio was not obtained, still in three instances it was obtained within the limits of possible error; once at 80° C., once at a lower temperature, and once at 130° C., with dilute acid.

The actual ratios found being—

$$2 : 2{\cdot}914$$
$$2 : 2{\cdot}964,$$

besides other instances in which this ratio was nearly attained, but in no case was a higher ratio for copper as sulphide to that of sulphate than 2 : 3 observed.

TABLE I. *Showing the Influence of Temperature.**

Temperature.	Time allowed.	Percentage proportion of Copper converted into		Percentage composition of insoluble residue.			Percentage of Copper dissolved.	Percentage of copper dissolved in one minute.
		Cu_2S.	$CuSO_4$.	Cu_2S.	CuS.	S.		
1. 19° C.	14 days	17·33	83·67	100	0	0	5·7	0·0003
2. 60	120 min.	5·25	94·75	100	0	0	2·532	0·0211
3. 80	30 min.	30·20	69·80	100	0	0	1·503	0·0501
4. 100	30 min.	25·00	75·00	100	0	0	3·123	0·1041
5. 124	30 min.	21·53	78·47	100	0	0	22·7	0·76
6. 130	30 min.	17·60	82·40	100	0	0	32·6	1·09
7. 137	30 min.	17·00	83·00	100	0	0	35·0	1·17
8. 150	30 min.	13·27	86·73	100	0	0	69·2	2·31
9. 170	10 min.	10·82	89·18	100	0	0	51·92	5·19
10. 195	2 min.	8·00	98·00	100	0	0	53·5	26·75
11. 220	0·5 min.	7·16	92·84	100	0	0	70·57	70·57 dissolved in ½ minute
12. 270	a few seconds	0	100·00	100	0	0	nearly 100·0	—
13. 170	30 min.	11·53	88·47	0	95·83	4·17	100·0	—
14. 195	30 min.	7·20	92·80	0	90·00	10·00	100·0	—
15. 220	30 min.	2·136	97·864	0	97·00	3·00	100·0	—

* Columns 3 and 4 in this Table, 4 and 5 in Table II, and corresponding columns in other tables, showing the proportion of copper converted into sulphide to that converted into sulphate, are made out so as to show the amount of copper originally as subsulphide calculated from the amount of subsulphide, protosulphide, and free sulphur (see secondary actions) found in the liquid at the conclusion of the experiments.

The combination of these two primary reactions, of which the one takes place alone at high temperatures only, the other only at low temperatures, explains all the results obtained at various intermediate temperatures, as given in the first twelve analyses of Table I, and equations can easily be formed representing the action in any given case; thus the following equations represent approximately the actions which take place at 100°, 130°, and 170° C. respectively.

$$8Cu + 10H_2SO_4 = Cu_2S + 6CuSO_4 + 3SO_2 + 10H_2O,$$
$$11Cu + 16H_2SO_4 = Cu_2S + 9CuSO_4 + 6SO_2 + 16H_2O,$$
$$24Cu + 42H_2SO_4 = Cu_2S + 22CuSO_4 + 19SO_2 + 42H_2O.$$

§ VI. *Secondary Actions.*

Thel ast three results given in Table I were those obtained originally at the temperatures 170°, 195°, and 220° C., in all of which cases the whole of the copper had been attacked before the time allowed for the experiment had expired, thus better opportunity for secondary reactions was afforded. It will be seen that in none of these cases was there any of the subsulphide left which had been proved by experiments given higher up in the table to have been first formed in each case, but in its stead a mixture of copper protosulphide and free sulphur, and in other cases, not given in the table, protosulphide only, or a mixture of the protosulphide and subsulphide was found. In order to ascertain whether the formation of these products was explicable by the decomposition of the subsulphide at first formed by the excess of hydrogen sulphate present, some of the sulphides were prepared by the ordinary methods, analysed, and then decomposed by heating with strong sulphuric acid.

The protosulphide was attacked by the acid at a temperature as low as 100°C., and was found by quantitative experiments to break up in the following manner:—

$$CuS + 2H_2SO_4 = S + CuSO_4 + 2H_2O + SO_2.$$

This may be regarded as consisting of the following stages—

(1.) $CuS + H_2SO_4 = CuSO_4 + S + 2H$,
(2.) $S + 2H = H_2S$,
(3.) $H_2S + H_2SO_4 = SO_2 + 2H_2O + S$,

but it seems to be more probable that the second molecule of hydrogen sulphate is decomposed directly by the nascent hydrogen, as in the main action of copper on the acid, thus—

(2.) $H_2SO_4 + 2H = SO_2 + 2H_2O$,

and not by the intervening formation of hydrogen sulphide, because

(*a.*) The hydrogen sulphide if formed would probably react on the copper sulphate instead of on the acid.

(*b.*) Hydrogen sulphide does not react on hydrogen sulphate at moderately high temperatures with great energy, and therefore a considerable portion of it would probably be evolved free from the liquid, whereas in reality no traces of it could be detected.

For these reasons it is therefore more rational to regard the steps constituting this reaction to be—

$$(1.)\ CuS + H_2SO_4 = CuSO_4 + S + 2H,$$
$$(2.)\ 2H + H_2SO_4 = SO_2 + 2H_2O.$$

The subsulphide was attacked by hydrogen sulphate at temperatures below 100°, breaking up first into the protosulphide, and forming at the same time copper sulphate, sulphur dioxide, and water, thus:—

$$(1.)\ Cu_2S + H_2SO_4 = CuS + CuSO_4 + 2H,$$
$$(2.)\ 2H + H_2SO_4 = 2H_2O + SO_2,$$

and then, after the whole of the subsulphide had been decomposed in this manner, the protosulphide formed by its decomposition was further broken up with formation of sulphate, and liberation of sulphur dioxide and free sulphur, as shown above.

These decompositions of the protosulphide by the excess of acid present explain all the results obtained in every experiment; and in various cases every step in the decomposition was traced, some of which will be found in the tables below, namely, cases in which

The copper was not entirely dissolved, and the black residue consisted entirely of subsulphide.

The copper was only just dissolved, and none of the subsulphide had been attacked.

The copper was entirely dissolved, and varying proportions of the subsulphide also, leaving a mixture of the two sulphides.

The copper was entirely dissolved, and the subsulphide just converted altogether into protosulphide.

The copper and subsulphide were entirely dissolved, and also the protosulphide to varying extents.

The copper and both the sulphides were dissolved, and nothing but sulphur left in the liquid.

§ VII. *Formation of the Sulphide.*

The following are arguments:—

(*a.*) That the sulphide is not formed by the action of *nascent hydrogen*—

(1.) If the subsulphide was produced by the action of nascent hy-

University of Michigan

drogen on the copper sulphate, it would be according to the following equations—

(1.) $6Cu + 6H_2SO_4 = 6CuSO_4 + 12H$,
(2.) $12H + 2CuSO_4 = Cu_2S + SO_2 + 6H_2O$,

in which case the greatest possible ratio which the copper converted into subsulphide could bear to that converted into sulphate would be 2 : 4, whereas the ratio 2 : 3 is obtainable.

(2.) If nascent hydrogen could react simultaneously on copper and copper sulphate, it would be according to the equation—

$$5Cu + 4H_2SO_4 = 3CuSO_4 + Cu_2S + 4H_2O,$$

this equation being then composed of two steps.

(1.) $4Cu + 4H_2SO_4 = 4CuSO_5 + 8H$,
(2.) $8H + Cu + CuSO_4 = Cu_2S + 4H_2O$.

But that nascent hydrogen cannot react in this way may be proved by treating a piece of zinc with dilute hydrogen sulphate mixed with a solution of copper sulphate, in which case no trace of copper subsulphide is formed, although hydrogen is here liberated in the nascent state in presence of metallic copper and copper sulphate.

(*b.*) That the sulphide is not formed by the action of *hydrogen sulphide*:—

(1.) Some hydrogen sulphide would in all probability be given off as such from the liquid, and its presence would have been easily recognised by the solution of silver nitrate.

(2.) The hydrogen sulphide would be formed by the previous liberation of nascent hydrogen, and the subsequent reaction of this body either on the hydrogen sulphate, or on the copper sulphate; if on the hydrogen sulphate the reactions would be represented by the following formulæ:—

(1.) $8Cu + 8CuSO_4 = 8CuSO_4 + 16H$,
(2.) $12H + 3H_2SO_4 = H_2S + 2SO_2 + 8H_2O$,
(3.) $H_2S + 4H + 2CuSO_4 = Cu_2S + H_2SO_4 + SO_2 + 2H_2O$,

and if on the copper sulphate by the formulæ—

(1.) $11Cu + 11H_2SO_4 = 11CuSO_4 + 22H$,
(2.) $18H + 2CuSO_4 = H_2S + Cu_2S + 8H_2O$,
(3.) $H_2S + 4H + 2CuSO_4 = Cu_2S + H_2SO_4 + SO_2 + 2H_2O$.

In the former of these cases the greatest proportion which the copper as subsulphide could bear to that as sulphate would be 4 : 12, and in the latter 4 : 7, whereas in reality the proportion 4 : 6 is obtainable.

(3.) Hydrogen sulphide reacts on copper sulphate, forming copper protosulphide and not subsulphide, which latter is the product obtained in the action in question.

(4.) The subsulphide is apparently formed on the surface of the copper, and not by the passage of bubbles of gas through the liquid.

(*c.*) That the sulphide is not formed by the union of the metallic copper with *free sulphur* previously liberated during the action, as stated by Calvert and Johnson.

(1.) Since the formation of hydrogen sulphide is untenable, the sulphur could only be liberated by the action of nascent hydrogen on the hydrogen sulphate or sulphur dioxide present, both of which reactions are improbable and unsupported by fact.

(2.) No sulphur is ever found in the insoluble residue produced during the action of hydrogen sulphate on copper till after the decomposition of the copper sulphides, and all the experiments performed on the subject prove that this sulphur, so far from being the cause of their formation, is in reality the product of their decomposition.

(3.) If the sulphide was formed by the combination of the copper with free sulphur, the amount of it produced would be increased by increasing the quantity of that sulphur; but this was proved not to be the case by adding a weighed quantity of sulphur to the acid used in one of the experiments; after the conclusion of the experiment the sulphur which had been added was not appreciably diminished in weight, nor was the quantity of copper sulphide formed greater than in other similar experiments where no sulphur had been added to the liquid. (It is sometimes stated in text books that sulphur, when suspended in a liquid, as obtained in the preparation of pentathionic acid, may be precipitated as copper sulphide by agitation with copper turnings, as if the metal combined directly with the sulphur. But the sulphur is in reality carried down with copper sulphide formed by the decomposition of copper pentathionate, as shown by Wackenroder, who proposed this method.)

We may therefore conclude that the sulphide cannot be formed in the way supposed by Calvert and Johnson, nor by the action of nascent hydrogen or hydrogen sulphide, but that the hydrogen sulphate is decomposed by the copper directly, forming copper subsulphide, &c.

In several experiments, where only a mere trace of copper was left unattacked, none of the subsulphide was decomposed, the reason being obvious, namely, that the acid would continue to act on the copper as long as any of this latter remained in the free state, and that not till after all the free metal had been dissolved would it attack the sulphide, it being much easier for the acid to combine with the

copper in the free state than to decompose a compound body containing it, and then combine with the liberated metal. The temperature at which these experiments were performed was above 170° C., *i.e.*, at a temperature when the brisk evolution of gas would prevent the metallic surface from becoming so densely coated by the deposition of subsulphide and sulphate as to protect it from the action of the acid; it was therefore anticipated that at lower temperatures, when the evolution of gas was slow, the coating of subsulphide and sulphate might be deposited so compactly on the copper that it would protect it entirely, or to a great extent, from the action of the acid, which would then be at liberty to attack the subsulphide. This anticipation was realised by a number of experiments performed at various temperatures, and for various lengths of time, some of which are shown in Table II. The protective effect of the coating of sulphide is shown in columns 6, 7, and 8, where it will be seen that the amount of subsulphide decomposed increases with the duration of the experiment, and it is also shown in the last four experiments, in column 9, where the amount of copper dissolved during successive intervals of thirty minutes is given. (In this column the first three experiments appear to give evidence contradictory to that afforded by the last four, but this will be satisfactorily explained below, p. 128).

TABLE II.

Temperature.	Time allowed.	Percentage of Copper dissolved.	Proportion of Copper converted into		Percentage composition of the insoluble residue.			Copper dissolved in consecutive intervals of 30 minutes.
			Cu_2S.	$CuSO_4$.	Cu_2S.	CuS.	S.	
1. 100° C.	30 min.	3·336	—	—	100	0	0	3·336
2. 100	90 min.	13·31	18·60	81·4	59·0	41·0	0	4·987
3. 100	120 min.	18·94	18·14	81·86	51·0	49·0	0	5·630
4. 137	30 min.	40·20	—	—	100·0	0	0	40·20
5. 137	60 min.	65·82	18·64	81·36	90·6	9·4	0	25·62
6. 137	90 min.	85·67	16·00	84·00	72·1	27·9	0	19·85
7. 137	120 min.	99·50	8·60	91·4	31·16	68·84	0	13·83

§ VIII. *Proportion of Acid to Metal.*

The amount of copper dissolved and the relative amount of sulphide formed are apparently not influenced by the proportion of acid and metal used when these are varied. Thus experiments were made with 1 part of copper to 0·6, 5·0, 10·0, and 20·0 parts of acid, but the means of many results obtained with these several proportions did not vary in any definite direction, or differ from each to a greater extent

than did the results of single experiments in which the same proportions of metal and acid were employed.

§ IX. *The Water formed.*

After the action is over, the acid is found to contain no copper sulphate in solution, though, water being formed during the action, it might be thought at first that some of the sulphate would certainly be dissolved, since this body is soluble in dilute though not in strong acid. But the fact is, that with the proportion of metal and acid used in most of the experiments, the water given off would be too insignificant to alter the density of the acid to any considerable degree. Thus, supposing that the action in which most water is formed with a given weight of copper, namely,

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O,$$

to take place only, and that the whole of the copper in the experiment were dissolved, the diminution in the density of the acid, as found experimentally, would only amount to about 0·008. Even a very small proportion of this water is given off at temperatures below 150° C., as was found by connecting a weighed calcium chloride drying tube with the flask, taking care after the experiment to expel the sulphur dioxide by a current of dried air. This increase in weight of the drying tube might possibly have been due to the spray of the acid carried off in the current of gas; but as the evolution of gas was very gentle, and as in other experiments the acid was not found to have experienced quite the theoretical diminution in density, it is probable that it was principally due to the water formed during the action. At higher temperatures more water is given off, and it makes its appearance in minute drops in the neck of the flask and in the delivery tube. In addition to there being more action, and therefore more water formed at higher temperatures, its volatilisation would be augmented by the increased evolution of gas. It was at first thought possible that owing to the great hygroscopic powers of anhydrous copper sulphate, that this salt might retain the water and form partially hydrated crystals, but this does not appear to be the case, because—

(1.) The crystals which separate out on cooling are perfectly white, like anhydrous copper sulphate, and do not exhibit any trace of a blue colour as do all its hydrated salts.

(2.) It was found by experiment that when copper sulphate containing even 1 molecule of water of crystallisation only, was heated with strong hydrogen sulphate, that it entirely gave up its water to the acid, this latter becoming diluted to a corresponding degree, and the copper sulphate crystallising out in white anhydrous crystals.

That the acid retained most of the water liberated in the majority of my experiments, is proved not only by the slight diminution of density observable at the conclusion of the experiment, but also by the fact already noticed, that the acid generally boils at a temperature a little below the boiling point of perfectly pure hydrogen sulphate.

§ X. *The Hydrogen Sulphate used.*

Some experiments were made to see if the acid actually entering into the reaction agreed with the amount required by the equation. The percentage of true acid in the hydrogen sulphate employed was first determined both volumetrically, by a freshly-prepared standard solution of ammonia, and gravimetrically, as barium sulphate. A weighed quantity of the acid was then heated, as in other cases, with a weighed quantity of copper. After the time allowed had expired, the acid was diluted and boiled in a current of carbon dioxide to free it from sulphur dioxide. In order to prevent any acid from being carried off during boiling, the delivery tube dipped into another flask containing a little water, and this second flask was similarly connected with a third flask, the contents of both of which were boiled in turn to free them from sulphur dioxide.* The loss in weight experienced by the copper and the amount of copper sulphide formed were then ascertained, from which data the equation representing the reaction which had taken place was constructed. The residual hydrogen sulphate was afterwards determined and found to agree, within experimental error, with that required by this equation. Several determinations were made, all of which gave satisfactory results.

§ XI. *Determination of the Sulphur Dioxide.*

The sulphur dioxide evolved was then determined. The equation was first constructed from the amount of copper attacked, and the amount of sulphide formed; the gas, eliminated from the liquid by boiling as in the determination of the hydrogen sulphate, was collected in a large volume of water carefully freed from air by long boiling, a

* Before the determination of the hydrogen sulphate, preliminary experiments were made, by which it was ascertained—

(1.) That boiling about 100 c.c. of a saturated solution of sulphur dioxide for 30 minutes in a current of carbon dioxide, was amply sufficient to free it from all traces of the former gas.

(2.) That the two washing flasks were necessary, but also sufficient, to prevent any loss of acid from the experimental flask.

(3.) That the copper sulphides were not appreciably decomposed by boiling in weak hydrogen sulphate (1 vol. of acid to 10 vols. of water being the proportion used) for 30 minutes, the liquid and apparatus being freed from air and filled with carbon dioxide.

current of carbon dioxide being drawn through the apparatus during the experiment. The sulphur dioxide thus liberated and collected was determined either gravimetrically, as barium sulphate after oxidation by means of bromine, or volumetrically, by standard solutions of iodine and sodium hyposulphite. Good results were obtained in this case also, two of which are given below. In the first of these the primary reactions alone took place, the black residue consisting entirely of copper subsulphide; in the second, all the primary, secondary, and tertiary actions had occurred, the residue consisting of copper protosulphide and free sulphur.

I. SO_2 required (as determined by copper dissolved and copper subsulphide formed) ..... = 0·06517 gram.
SO_2 found ..... = 0·06513 gram.
= 99·94 per cent.

II. SO_2 required (as determined by the copper dissolved and the persulphide and sulphur formed) ..... = 0·3419 gram.
SO_2 found ..... = 0·3364 gram.
= 98·363 per cent.*

Thus having determined accurately every factor (with the exception of the water, and that necessarily only approximately) on both sides of the equation representing the action of hydrogen sulphate on copper, and the secondary action entailed by it, and finding these determinations to agree perfectly with the explanation above given of this action, there can be little doubt that this explanation is correct, and that the explanations given by others, to be discussed below, are incorrect, since, if otherwise, in none of these cases could the factors be what experiment shows they really are.

§ XII. *The Sublimate of Sulphur.*

The appearance of a small sublimate of sulphur in the neck of the flask, and in some cases in the delivery tube, occurred as already mentioned, only after the complete solution of the copper; and since its formation was also observed on decomposing the sulphides of copper by hydrogen sulphate, we may conclude that it owes its origin to this latter action, and not to either of the primary reactions. Now, since no hydrogen sulphide was detected by the silver nitrate solution as being liberated during the decomposition of the sulphides, this sulphur

* Both of these results are within the limits of experimental error. In the second one, owing to the necessarily small quantity of copper taken and small quantity of the insoluble residue obtained, a very small error in the determination of the free sulphur would account for the difference of 1·64 per cent. obtained.

could not have been formed by the mutual reaction of the hydrogen sulphide on the sulphur dioxide. This may at first sight appear a false argument, but in observing other similar reactions, such as the decomposition of tetrathionates by hydrogen chloride, in which the main gaseous product is sulphur dioxide, a small quantity of hydrogen sulphide being liberated together with it, it is seen that a comparatively small deposition of sulphur is accompanied by a comparatively large indication of hydrogen sulphide in a silver solution, into which the delivery tube is made to dip. Therefore, the formation of the sulphur sublimate in the copper action may be more reasonably attributed to a cause which must inevitably come into play, namely, the volatility and tendency to creep up the sides of the containing vessel exhibited by sulphur when in a state of fine division. This is supported by the fact, that the sublimate is visible in the neck of the flask in greater quantities, and long before it is visible in the delivery tube, and in this latter only at high temperatures; whereas, owing to the comparative narrowness of the tube, if formed by the reaction of two gases on each other, it would, as in the decomposition of the polythionates, show itself sooner and in greater quantities here, where the gases are brought into closer proximity with each other. It is more probable that the free sulphur is expelled from the liquid, chiefly owing to its tendency to creep up the sides of the containing vessel, and not to its volatility, because when a compact piece of sulphur is heated with hydrogen sulphate, none of it sublimes till some time after that in the liquid has attained its melting point; whereas, if sulphur in the finely-divided state is employed, a deposit is observed in the neck of the flask as low as 110° C. Still sulphur is volatile to a certain extent, even at 100° C., especially when its volatilisation is aided by the evolution of a gas or vapour in proximity to it, as shown by the notable smell of this body, perceived when drying a precipitate containing it in a steam bath, or when boiling liquids in which it is suspended.

§ XIII. *Influence of an Electric Current.*

The influence of an electric current on copper, while being acted on by hydrogen sulphate, was then tried, chiefly with a view of ascertaining whether the relative amount of copper sulphide and sulphate formed would thus be altered. This was done in two ways, either by connecting the copper with one of the plates of a small Daniell's cell, the other plate being connected by a platinum wire with a small piece of platinum foil immersed in the acid, or else the copper was made electropositive by simply attaching it to a piece of platinum wire coiled up, and entirely immersed with the copper in the acid. Of

course the more electropositive the copper was made, the more of it was dissolved in a given time, and *vice versâ* (though the poles were not arranged so as to get the greatest amount of action); but in addition to this it was found that when the copper was electropositive, the proportion of sulphide to sulphate formed was increased, whereas when electronegative the proportion was diminished, as shown in Table III, where the means of many experiments are given. The diminution and increase in the proportion of sulphide to sulphate formed, according as the metal is made electronegative or electropositive respectively, is not great, but in all cases it varied in the same direction, though to a greater or less extent.

TABLE III. *Showing the Effect of an Electric Current.*

Temperature.	Time allowed.	Condition.	Percentage of Copper dissolved.	Percentage composition of the insoluble residue.			Proportion of Copper as		Percentage of Copper dissolved in consecutive intervals of 15 minutes.
				Cu_2S.	CuS.	S.	Cu_2S.	$CuSO_4$.	
1. 100° C.	30 min.	Positive	14·214	59·8	40·2	0	15·2	84·8	—
2. 100	30 min.	Ordinary	3·707	100	0	0	13·415	86·585	—
3. 100	30 min.	Negative	3·256	100	0	0	10·773	89·227	—
4. 100	15 min.	Positive	6·978	—	—	—	—	—	6·978
5. 100	30 min.	Positive	13·197	—	—	—	—	—	6·219
6. 100	60 min.	Positive	18·184	—	—	—	—	—	2·494

It will be observed that when the copper was made electropositive, the sulphide did not consist, as in other cases, of subsulphide only, but of a mixture of subsulphide and protosulphide. This is easily explained, thus: When the copper is made electropositive, as much metal is dissolved during the first 15 minutes as is dissolved in about one hour when it is not made electropositive or when made electronegative; and consequently in the former case as much or even more sulphide (since also the relative proportion of sulphide is increased) is formed, as in the latter case; but, as shown above, the amount of subsulphide formed during about one hour at 100° C. under ordinary conditions is sufficient to coat the copper to such an extent that it greatly protects the metal, and itself become attacked; consequently, when the copper is made electropositive, and the action proceeded with about four times its ordinary rapidity, we should expect, as is the case, that the sulphide will begin to be decomposed after about the first 15 minutes. The protective action of the sulphide is shown by the last three experiments given in Table III, where (in the last

column) a relatively smaller amount of action is seen to occur as the time allowed is longer. In order to make sure that, in these cases as well as in those already considered, the subsulphide was in reality the first product, and that the protosulphide owed its origin to the secondary reaction, and was not produced directly from the copper, experiments were made with copper rendered electropositive for 5, 10, and 15 minutes; always when 5 and 10 minutes, and sometimes when 15 minutes were allowed, the insoluble residue consisted entirely of subsulphide, showing that this was in reality the first product.

From the moderately good conducting power of copper sulphide, and the fact that being less easily attacked by hydrogen sulphate than metallic copper, it would act in an electronegative manner towards this latter body, it was thought probable that the sulphide as it was formed, by making the copper more electropositive, would increase the actual amount of action during the first stages. That this was in reality the case, was proved by performing several series of experiments at the same temperature with the same piece of copper (to make the several results more strictly comparable with each other, due corrections being made for the relative increase of surface exposed) for successively increasing intervals of time. Two of these series are given in Table IV, and these may also be taken in conjunction with those given in Table II, &c., as illustrative of the effect of time on the products of the action. The figures in the last column of this table

TABLE IV. *Showing the Action of the Sulphide on the Amount of Copper Dissolved.*

Temperature.	Time allowed.	Percentage of Copper dissolved.	Percentage composition of the insoluble residue.			Proportion of Copper as		Percentage of Copper dissolved in consecutive intervals of 5 minutes.
			Cu_2S.	CuS.	S.	Cu_2S.	$CuSO_4$	
1. 100° C.	5 min.	0·2001	100	0	0	—	—	0·2001
2. 100	10 „	0·834	100	0	0	9·6	90·4	0·634
3. 100	20 „	2·300	100	0	0	12·75	87·25	0·767
4. 100	30 „	3·336	100	0	0	—	—	0·901
5. 100	40 „	4·987	100	0	0	13·1	86·9	0·825
6. 100	50 „	7·171	100	0	0	17·3	82·7	1·093
7. 100	60 „	7·572	—	—	—	—	—	0·2005
8. 100	90 „	13·310	59·0	41·0	0	18·6	81·4	0·9565
9. 100	120 „	18·94	51·0	49·0	0	26·38	73·62	0·905
1. 100	5 „	0·513	—	—	—	—	—	0·513
2. 100	10 „	1·310	—	—	—	—	—	0·797
3. 100	20 „	3·574	—	—	—	—	—	1·132
4. 100	40 „	7·206	—	—	—	—	—	0·932
5. 100	60 „	9·072	—	—	—	—	—	0·442

show the additional quantities of copper dissolved in consecutive and equal increments of time, and it is thus seen that the amount dissolved increases rapidly at first, then more gradually, till after reaching a maximum, it begins to decrease, chiefly owing, as was said above in connection with other experiments, to the protective action of the coating of sulphide, and partially also to the increasing diminution in density of the acid, a very small diminution of which is capable, as will be shown below, of having considerable influence on the amount of copper attacked. In the series given in Table IV, the amount and composition of the sulphide formed was not determined with much accuracy, this being unnecessary, and indeed with the small amount of action in many cases it would have been impossible to do so; but, as might have been anticipated from the effect of making the metal electropositive by other means, the proportion of sulphide to sulphate increases with the amount of copper acted on, *i.e.*, with the actual amount of sulphide present.

(When the copper acted on is made the negative electrode, the platinum which acts as the positive electrode naturally remains bright, but when the current is reversed the negative electrode (*i.e.*, the platinum) becomes slowly coated with a black deposit, which, as far as can be judged by qualitative analysis (since sufficient of it was not obtained to admit of a quantitative determination), consists of copper sub-sulphide. This evidently arises from the deposition of metallic copper on the platinum which acts as the negative electrode, owing to the electrolysis of the copper sulphate in the liquid; the copper thus deposited soon becomes attacked by the acid in the same way as, but to a smaller extent than, the copper constituting the positive electrode, thus giving rise to a film of copper sulphide covering the platinum. The prior deposition of the metal may be observed by taking a bright piece of copper, coating one half of it with mercury, and then immersing it, without connecting it with the battery, in heated hydrogen sulphate; almost as soon as the exposed copper begins to be attacked the mercury, acting as a negative electrode, becomes coated with a thin film of metallic copper, and if the acid be poured off before the action has proceeded too far, this deposit will exhibit most beautifully the colours of thin films, in which, owing to the natural colour of the copper, rich purple and magenta tints prevail. If left in the acid this film soon becomes reddish, and finally black, consisting then of copper sulphide. These colours first exhibited by the film would prove that a deposition of a layer of metallic copper must be the origin of the coating of copper sulphide on the platinum or mercury, since no such colour can be seen during the deposition of sulphide on uncoated copper, and it is indeed impossible to see how any copper subsulphide could be otherwise deposited on the negative electrode.)

§ XIV. *Influence of Purity.*

(*a.*) *Of the Metal.*—The influence of the purity of the metal used was then studied. The copper employed in the above experiments, as already mentioned, was ordinarily pure electrotype foil, and the usual tests failed to detect any metallic impurities in it. Some commercial sheet copper was then taken, containing small quantities of arsenic, tin, silver, iron, and lead, and substituted for the electrotype metal; the mean of several experiments with the impure metal is given in Table V, 5, comparable with 2 of the same table, results which were obtained with the pure metal under similar circumstances.

TABLE V. *Showing the Influence of Impurity in the Copper.*

Quality of Sample.	Temperature.	Time allowed.	Percentage composition of the insoluble residue.			Proportion of Copper as		Percentage of Copper dissolved.
			Cu_2S.	CuS.	S.	Cu_2S.	$CuSO_4$	
1. Purest electrotype wire	100° C.	30 min.	100	0	0	—	—	2·412
2. Pure electrotype foil.....	100	30 „	100	0	0	16·592	83·408	3·123
3. Less pure electrotype foil ..	100	30 „	100	0	0	—	—	4·068
4. Copper binding wire	100	30 „	—	—	—	—	—	4·897
5. Commercial sheet copper..	100	30 „	83·3	16·7	0	22·0	78·0	11·5
6. A bronze coin..	100	30 „	—	—	—	—	—	14·8
7. Copper turnings (very impure)	100	30 „	—	—	—	—	—	17·226

The main points that will be noticed in the experiments performed with the common metal are, firstly, that the insoluble residue does not consist of the subsulphide only, but of a mixture of the two sulphides, and, secondly, that a far greater amount of the metal is attacked than when pure copper is used. The former of these two results is a consequence of the latter, being explicable in the same manner as when an increase in the amount of action is produced by making the metal electropositive, namely, that sufficient sulphide is formed in the first part of the reaction to protect the metal considerably from the acid, and thus the subsulphide itself becomes attacked before the action has proceeded far. In this case, as in the others, it was proved by making the experiment last only 10 or 15 minutes, that the first product was invariably copper subsulphide only. The reason why much more copper should be dissolved in a given time when im-

pure than when pure is not so obvious. From the near accordance of the amount of impure metal dissolved with the amount of pure metal dissolved, when rendered electropositive, I thought at first to attribute the increase of action obtained when the metal is impure, to its being made electropositive by the metallic impurities present in it; but it was found that this explanation would not hold good, from the following consideration:—Faraday has shown that the metals which exist as impurities in commercial copper, namely, lead, tin, bismuth, iron, antimony,* and silver are, with the exception of this last-named metal, electropositive towards copper in weak hydrogen sulphate, silver being electronegative towards it; and, as far as can be judged from rough experiments, these metals hold nearly the same position in the electrochemical series towards copper when the liquid is strong hydrogen sulphate at a temperature of 150° C.; arsenic and silver being electronegative towards copper, since it is improbable that the small traces of arsenic and silver in commercial copper should so entirely counteract the effect of all the other impurities present as to render the metal decidedly electropositive, we should expect to find impure copper less electropositive than pure copper towards hydrogen sulphate. The following facts show that this is in reality the case. When copper, either pure or impure, is acted on by sulphuric acid, it is found to be in a more electronegative than electropositive condition, for the increase in action when made electropositive is much greater than the decrease when made electronegative. But when pure the increase when made electropositive is $\frac{3 \cdot 84}{1 \cdot 0}$ and the decrease when made electropositive is $\frac{0 \cdot 8553}{1 \cdot 0}$, whereas when impure the increase in action $\frac{7 \cdot 75}{1 \cdot 0}$ and the decrease $\frac{0 \cdot 96}{1 \cdot 0}$, the impure being obviously more strongly electronegative than the pure, and therefore the increase of action caused by the presence of impurity in the copper cannot be attributed to the galvanic influence of that impurity.

In addition to the two main points noticed as above, in connection with the purity of the copper, it will also be seen that the relative proportion of sulphide formed is rather greater when the metal is impure than when pure. I can give no satisfactory explanation of this, and can only state that at the same temperature the relative amount of sulphide formed increases slowly with the amount of metal acted on; and it would follow from this that the proportional increase of sulphide observed when pure copper is rendered electropositive, and *vice versâ*, is not due to the fact of the metal being in a certain electrical condition, but merely to the increased or diminished amount of action owing to that electrical condition.

* Faraday did not experiment on arsenic, which is also a common impurity in copper, but it seems to be electronegative towards copper and electropositive towards silver in hydrogen sulphate either strong or weak.

The increased relative amount of sulphide formed with impure copper is also seen by its forming a notable amount of sulphide at 270° C., when the pure metal forms none. Pure copper also when rendered electropositive by being attached to a platinum wire also forms an easily distinguishable amount of sulphide at 270° C. The best mode of observing it is to string the pieces of copper on to a loop of platinum wire fused into a glass rod; this may be passed through a hole in the cork closing the tube or flask used, and gradually lowered into the acid when it has attained the required temperature; the action is thus rendered manageable, and the escaping gas may be conducted away through a delivery tube and be absorbed.

On examining the piece of copper after it has been attacked by the acid, it is found that when impure the surface is far more rough and uneven than when pure, showing that in the former case the action has been very unequal in contiguous parts owing to the presence of impurities. The coating which the sulphides (afterwards becoming attacked and being replaced by sulphur), together with the anhydrous sulphate forms, first in the rugosities, and then over the whole surface, is naturally much more compact than when formed on the even surface retained by pure metal throughout the action, so much so that after a certain amount of metal has been dissolved, the remainder is almost completely shielded from the acid and remains unattacked, even after prolonged immersion in the acid at moderately high temperatures.

This protective action of the sulphide deposited on impure copper may be shown by the following experiment:—A piece of impure copper is immersed in acid in contact with a piece of pure metal, both pieces exposing equal surfaces; being in contact, the effect is the same as if the impurity were equally divided between both pieces, and each should be acted on to the same extent, but it is found that the *pure* metal is invariably most attacked, showing that the impure must have been protected to a greater extent than the pure by the coating of sulphide.

Other samples of copper were experimented with, and an average of the results obtained with each is given in Table V.* The results obtained at higher temperatures agreed in the several instances with those obtained at 100° C. which are here given. They are arranged, beginning with samples which gave the least amount of action, and ending with those that gave the most, and the order thus obtained is, as far as can be judged without accurate quantitative analyses of each

* The results given in the table are corrected so as to exhibit the amount of action obtained with equal weights exposing equal surfaces to the acid, this being the only way in which experiments performed with samples of various thicknesses can be rendered comparable.

sample, the same, on the whole, as that which would be obtained by arranging the metals according to their relative purity, the greater being the amount of action according as the amount of impurity is greater. (The coin probably contained a considerably smaller percentage of copper than the turnings, but it owes its position in the table to the zinc present in it, which would act electronegatively in the strong acid, and therefore in opposition to the other impurities.) This fact, and the fact that a very small amount of impurity is capable of causing a great increase in action, leads to the conjecture that if such a thing as perfectly pure copper could be obtained, it might not be acted on at all by hydrogen sulphate, but from the impossibility of obtaining absolute purity this must, for the present, remain but a mere conjecture.

(*b.*) *Of the Acid.*—The usual amount of impurity in commercial hydrogen sulphate is too minute to have any appreciable effect on the action; but if the arsenic usually present in it be increased in amount, it becomes deposited on the copper, and, being electronegative towards it, increases the action.* If the amount of lead is increased no alteration is caused in the action, since lead is electropositive towards copper in hydrogen sulphate.

§ XV. *Action with Dilute Acids.*

Table VI exhibits the influence of diluting the acid employed in the experiments; it will be seen from it that the amount of action decreases rapidly with the decrease in density of the hydrogen sulphate. The amount of copper dissolved during the time allowed—30 minutes—began to be appreciable at 130° C. with the acid H_2SO_4,H_2O, and at 165° C. with the acid $H_2SO_4,2H_2O$; though probably if the time allowed was much prolonged an appreciable action would take place at considerably lower temperatures, since the amount of action obtained with the stronger acid at 130° C., and with the weaker one at 165° C., is about equivalent to that obtained with pure acid at 100° C. No appreciable action was obtained with acid weaker than $H_2SO_2,2H_2O$. The composition and quantity of sulphide formed agreed with the composition and quantity of it formed by strong acid at such temperatures when equal amounts of copper were acted on.

The results given in Table VI agree with those obtained by Calvert and Johnson, as near as can be expected, considering what minute differences in the purity of the metal and dilution of the acid alter to a great extent the amount of action.

* Reinsch's test may thus be effectually performed in hydrogen sulphate even when weak, though it is far less quick in operation than when the liquid used is hydrogen chloride.

TABLE VI. *Showing the Action of Acid of Various Strengths.*

Temperature.	Time allowed.	Acid used.	Density.	Percentage of Copper dissolved.	Proportion dissolved to that dissolved by acid sp. gr. 1·843 at the same temperature and for the same length of time.
1. 100° C.	30 min.	H_2SO_4	1·843	2·380	1 : 1
2. 100	30 „	$H_2SO_4,2H_2O$	1·8295	0·585	0·246 : 1
3. 100	30 „	H_2SO_4,H_2O	1·780	0	0 : 1
4. 100	30 „	$H_2SO_4,2H_2O$	1·620	0	0 : 1
5. 130	30 „	H_2SO_4	1·843	32·6	1 : 1
6. 130	30 „	H_2SO_4,H_2O	1·780	1·182	0·0363 : 1
7. 130	30 „	$H_2SO_4,2H_2O$	1·620	0	0 : 1
8. 165	30 „	H_2SO_4	1·843	70 in 15 min.	1 : 1
9. 165	30 „	H_2SO_4,H_2O	1·780	16·54	0·11 : 1
10. 165	30 „	$H_2SO_4,2H_2O$	1·620	2·744	0·018 : 1

§ XVI. *Variation of Results.*

The experiments given in the above table are either means of a large number, or else characteristic results selected from several. It would be superfluous to give the results of more experiments than are here given, since they all bear the same evidence as to the nature of the action and the circumstances which influence it.

Often in comparing together several results of experiments, performed as nearly as possible under similar circumstances, considerable variation on either side of the mean was observed. From what has been said above, it is not difficult to see that this would naturally be the case from the minute and unavoidable circumstances which influence the action, namely :—

(1.) A very slight change in the density of the acid.

(2.) A minute alteration in the amount or kind of impurity in the metal, so small that different, though contiguous pieces of the same sample of metal may give considerably different results, as is shown by the greater concordance observed when several similar experiments are performed with the same piece of metal than when performed with different pieces of the same sample.

(3.) The mode in which the sulphide is deposited; since a small alteration in temperature, or in the purity of the metal, makes a considerable difference in the compactness of the film.

(4.) The mode in which the pieces of copper are placed in the liquid; since it appears that between two pieces touching each other, the film of sulphide and sulphate is deposited so compactly as to make them adhere together. (The pieces of copper which have been in contact with each other are invariably thicker after the action than

those which have not been in contact, and also, on the former, the sulphide leaves a darker and more indelible stain than on the latter.)

(5.) The difficulty of keeping the temperature of the bath exactly constant for any length of time, except the temperature employed be 100° C.

(6.) And lastly, the fact that the thickness of the copper varies sufficiently (especially when it is in foil, as in the majority of the above cases) to cause the same weights of it to show considerably different amounts of surface.

But in spite of the impossibility of getting very accurate and concordant results, by performing a number of experiments in each case,* sufficient concordance is obtained to leave no doubt whatever as to the true reaction.

The amount of variation may be seen in Table VII (and indeed in most of the previous tables), where the extreme results obtained in a few classes of experiments are given.

TABLE VII. *Showing Extent of Variation of Results.*

Copper used.	Temperature.	Time allowed.	Percentage of Copper dissolved.	Percentage composition of insoluble residue.		Proportion of Copper as	
				Cu_2S.	CuS.	Cu_2S.	$CuSO_4$
1. Pure † 2. Pure †	100° C. 100	30 min. 30 „	2·486 2·38	— —	— —	— —	— —
3. Pure	100	30 „	3·932	—	—	14·58	85·42
4. Pure	100	30 „	1·445	—	—	18·18	81·82
5. Pure	137	90 „	97·0	90·6	9·4	18·12	81·88
6. Pure	137	90 „	85·6	72·1	27·9	16·00	84·00
7. Impure † 8. Impure †....	100 100	30 „ 30 „	9·92 9·924	— —	— —	— —	— —
9. Impure	100	30 „	14·051	—	—	—	—

§ XVII. *Other Opinions as to the Action.*

The explanation of the action of sulphuric acid on copper given above is at variance with those already given by others who have studied the reaction.

Berzelius (*Traité de Chimie*, iv, 324) mentions the formation of a black insoluble powder, oxidisable by hydrogen nitrate, and which

* I have performed about 250 experiments on this subject.

† Same piece of copper used in both experiments.

University of Michigan

"appears to be" copper subsulphate, though this body requires only 56·76 per cent. of copper, whereas the copper in the residue after the extraction of free sulphur is never less than 66·316 per cent., in addition to which recent experiments show that copper subsulphate is a soluble and not an insoluble body.

Barruel (*Journ. de Pharm.*, xx, 13, 1834) showed that the action between copper and sulphuric acid takes place at ordinary temperatures if sufficient time be allowed; though he obtained a far smaller amount of action than that given in Table I. He states, as has also been noticed above, that at low temperatures the sulphur dioxide formed is dissolved in the liquid, and he considers that this reacts on the copper forming protosulphide and protoxide of copper, the latter afterwards dissolving in the acid. The only experiment which he adduced in support of this view, was to enclose some copper in a hermetically sealed tube with some sulphurous acid. After six months a brownish body appeared in the liquid, containing sulphur and copper, and which, there is no reason to doubt, was a sulphide of copper. But though sulphur dioxide in solution may attack copper under certain circumstances, still it is not difficult to prove that, in the action of sulphuric acid on copper, it does not do so to any appreciable extent, for if some copper be heated in an aqueous solution of hydrogen sulphite, and a constant current of sulphur dioxide be drawn through the liquid during the experiment, it will be found that the copper remains perfectly untarnished and unattacked, whereas under similar circumstances, but using hydrogen sulphate instead of hydrogen sulphite, a large amount of copper is found to have been dissolved and converted into sulphide. Barruel, like Berzelius, does not appear to have made any quantitative analyses of the black residue.

Maumené (*Ann. Chim. Phys.*, 1846, 3rd series, xviii, 311), after performing several analyses of the insoluble residue, arrived at the following conclusions as to its formation and composition:—

That, besides the main reaction forming copper sulphate, sulphur dioxide, &c., there is another distinct reaction, consisting of four distinct steps, and giving rise to four different bodies—

(1.) Copper subsulphide, Cu_2S.
(2.) An oxysulphide of copper, $CuO,2Cu_2S$, or Cu_5S_2O.
(3.) Another oxysulphide of copper, $CuO,2CuS$, or Cu_3S_2O.
(4.) Another oxysulphide of copper, CuO,CuS, or Cu_2SO.

The first of these steps, namely, the formation of the subsulphide, is the same as that which I consider takes place.

As regards the other steps, it is difficult to understand how Maumené failed to see that the percentage of copper and sulphur together invariably made up 100 per cent. of the black residue. The

explanation perhaps lies hid in an unintelligible passage which occurs in his paper (p. 316), in which he mentions that granulating the copper was an expedient which he used to render easy the separation of the oxysulphide from the unattacked copper, and at the same time to prevent any copper remaining unattacked. In the same passage he refers to a "matter insoluble in acids," which existed in large quantities in the copper turnings which he employed; this matter concentrated itself in the copper sulphides, increasing their weight by as much as one-twentieth, and in many of his analyses he made allowance for this, though, in what way, he does not state.

The first oxysulphide contains nearly the same percentage of copper as the subsulphide; the others contain percentages intermediate between that of the sulphide and protosulphide. Thus—

Cu_2S contains.....	Cu ..	79·814	S ..	20·186	O ..	0·0
$CuO.2Cu_2S$ contains	Cu ..	79·821	S ..	16·150	O ..	4·029
$CuO.2CuS$ „	Cu ..	70·356	S ..	23·726	O ..	5·918
$CuO.CuS$ „	Cu ..	72·511	S ..	18·339	O ..	9·150
CuS „	Cu ..	66·408	S ..	33·592	O ..	0·0

The last three steps which he considers to take place, suppose the formation of three bodies, the existence of which has never been proved, and is not supported even by the majority of his own analyses, as he says that the percentage of copper or sulphur required by the formulæ Cu_4S_2O, Cu_3S_2O, Cu_2SO, were never exactly obtained by him, and the strongest proof which he adduces for the formation of these bodies is the fact that Pelouze has shown the existence of a body, 5CuS,CuO. If Maumené had let the action continue longer, he would have ascertained that the last state of the residue is by no means one in which the copper amounts to as much as 72·414 per cent., but only to 66·316, and taking into consideration the free sulphur, which he does not appear to have recognised, indefinitely less.

In addition to the improbability of copper oxide being formed and remaining unattacked in presence of excess of strong hydrogen sulphate, the following experiment disproves its formation. A piece of copper, bent at right angles, was placed in a large watch-glass containing hydrogen sulphate, so that half the metal should be immersed in the acid and half should project into the air, the whole being placed under a bell-jar to prevent diminution in the density of the acid by absorption of moisture from the atmosphere; the portion of the metal in the air, being unacted on, or acted on only to a very small degree, performed the part of an electronegative metal towards the copper in the acid, which, becoming thus more electropositive, was acted on to a greatly increased extent (on an average about five times as much as if it was entirely immersed); and instead of the relative

proportion of sulphide formed being increased, as when rendered electropositive under other circumstances, it was greatly decreased, so that only a trace of it could be discerned. Now this could not be due to the fact of the copper being made electro-positive, since doing so *increases* the amount of sulphide; it must therefore have been due to the copper sulphide being oxidised at the time of its appearance by the oxygen which would be liberated at the surface of that portion of the copper which is immersed in the acid, since the whole arrangement would form a galvanic cell consisting of a metal, a liquid, and a gas. If, therefore, this black residue consists of, or contains copper oxide, it is wholly inconceivable that the action of more oxygen can diminish the amount of oxide formed, especially when this oxide, according to Maumené, is the peroxide. The fact that the presence of free oxygen will diminish the proportion of the insoluble residue, was also shown by acting on some copper, first with acid carefully freed from oxygen by boiling, and by passing a current of carbon dioxide through it, and then with acid through which a current of air was passed throughout the experiment, a larger proportion of sulphide being formed in the former than in the latter case.

The determinations of the sulphur dioxide made also give conclusive proof that the residue can contain no oxygen.

The fact, already noticed, that the sulphide is at first of a brownish colour, does not argue at all that any body besides the sulphide is formed, nor does Maumené consider it to do so, since he agrees with me, that, at the time when the brown colour is most conspicuous, the body consists undoubtedly of copper subsulphide only; the brown colour at first visible appears to be due merely to the smallness of the amount of the subsulphide present, which moreover is exactly similar to that produced by a small quantity of the protosulphide when suspended in a liquid. Unfortunately Maumené gives no particulars as to the circumstances under which his experiments were performed, so that they cannot be repeated.

Calvert and Johnson (*Journ. Chem. Soc.*, xix, 438, 1866), performed a few experiments on the relative effect of strong and dilute sulphuric acid on copper at temperatures of 130° amd 150° C., the results of which, as mentioned above, agree moderately well with those given on p. 134. They mention the formation of copper subsulphide, and consider it to be due to the liberation of free sulphur, which latter afterwards combines directly with the metal. This view they supported by no experiments on the subject or analyses of the sulphide, but held it for the following reasons:—

(1.) No hydrogen sulphide is evolved.

(2.) Sulphur is volatilised.

(3.) From the similarity between this action and that of sulphuric acid on tin.

The first two of these reasons have already been discussed, and much weight can scarcely be given to the last reason, when in the account of their experiments on the action of hydrogen sulphate on tin, given in the same paper, they state "that the action of various strengths of sulphuric acid upon tin differs entirely from that which they exert upon copper." They failed to obtain any action below 130° C., and considered that none took place, in spite of the fact that Barruel, as early as 1834, had proved that it took place even at ordinary atmospheric temperatures. Experiments detailed above show that the difference in action obtained at low temperatures (except indeed where the action $5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O$ alone takes place) up to 270° C. is one of degree only, and not of kind.

XVIII. *An Inquiry into the Action of the Copper-zinc Couple on Alkaline Oxy-salts.*

By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe, F.C.S., Lecturer on Chemistry in Dulwich College.

Part I.

In 1873 Professor Thorpe established the fact that the copper-zinc couple in presence of nitre and water converts the whole of the nitrogen of the salt into ammonia. Some months prior to the publication of his paper it had been noticed by ourselves that the couple quickly reduces an aqueous solution of this salt to nitrite of potassium.

This reduction first to nitrite, then to ammonia, is of considerable interest, and appeared to us to call for a more extended study. A close observation of the course of the chemical change we thought might reveal Dr. Diver's hyponitrite about which so little is known, and perhaps lead to the real explanation of this and similar reactions, about which nothing definite has yet been ascertained.

The couples used in this research were made by adding 100 c.c. of a 2 per cent. solution of copper sulphate twice to every meter of zinc foil 5 centimeters wide.

Potassium Nitrate.

We give the details of two experiments on the reduction of this salt. The nitrite and ammonia were each estimated daily at about the same

hour; the ammonia by the Nessler method, the nitrite by potassium permanganate.

In the first experiment 4 meters of foil were used, and 500 c.c. of a 1·2 per cent. solution of the salt; in the 2nd, 8 meters of foil and 640 c.c. of a 2·47 per cent. solution. The results are given below:—

Expt. I.

Time.	Temperature. Centigrade.	Percentages in grams.		Equal to KNO_3 reduced.	Work done each day expressed in milligrams of Hydrogen.*
		KNO_2.	NH_3.		
1 day	15°—17°	0·673	0·012	0·871 gram	107·8
3 days	„	0·820	0·025	1·123 „	23·3
4 „	„	0·778	0·03	1·103 „	6·6
5 „	„	0·704	0·0425	1·09 „	19·5
6 „	„	0·589	0·072	1·127 „	51·3
7 „	„	0·347	0·1212	1·132 „	78·6
7 days 12 hours ..	„	0·150	0·184	1·24 „	215
8 „	„	Nil	—	—	—

Expt. II.

4 hours	17	0·526	0·006	0·66 „	583·6
1 day	13	1·182	0·022	1·535 „	241·7
2 days	14	1·429	0·036	1·912 „	74·2
3 „	14·5	1·587	0·0456	2·157 „	47
4 „	14·5	1·587	0·07	2·302 „	62·5
5 „	15·5	0·758	0·256	2·422 „	342·4
5 days 6 hours ..	17	Nil	0·40	2·376 „	955·2

During the progress of the experiments, hyponitrite was tested for with silver nitrate twice daily, but in every case with a negative result. The amount of permanganate used up in the estimations during the latter part of the action, jointly with the ammonia formed, points not only to the non-formation of this hyponitrite, but also of any body requiring for its oxidation more permanganate than the nitrite.

The course of this chemical change is remarkable. It starts somewhat energetically, then diminishes considerably, again increases, and finally ends more rapidly than it began. Ammonia and its equivalent of potash increase but slowly from the commencement until the time when the maximum amount of nitrite is produced, when this salt rapidly gives way, accompanied of course by an increasing amount of

* Calculated in accordance with equations:—

(*a*.) $KNO_3 + H_2 = H_2O + KNO_2$,

(*b*.) $KNO_3 + H_8 = KHO + 2H_2O + NH_3$.

the alkalies. This rapid breaking down of the nitrite is coincident with the renewed activity of the couple, and it might therefore be thought that it is a consequence of the smaller stability of the nitrite; but this can scarcely be the explanation, since we see that almost from the very commencement the couple elects to deoxidise the nitrate, when it has the opportunity of attacking the nitrite.

The question therefore arises, are the variations in the amount of the action, especially the acceleration, due to the ammonia and potash produced? The following series of experiments show the influence of these bodies on the amount of hydrogen set free. The first column represents the hydrogen from a couple immersed in water alone; the second and third from similar couples immersed in similar volumes of aqueous solutions of NH_3 and KHO respectively. The strengths of the solutions of ammonia and potassium hydrate in each set of experiments approximate to the equivalent proportions. The gas measurements were taken after two hours.

In Expt. A, the strength of NH_3 used was 0·026 per cent.; KHO, 0·087 per cent.

In Expt. B, the strength of NH_3 used was ·0256 per cent.; KHO, 0·846 per cent.

In Expt. C, the strength of NH_3 used was 0·51 per cent.; KHO, 1·69 per cent.

In Expt. D, the strength of NH_3 used was 20·0 per cent.; KHO, 65·8 per cent.

Taking the action of the water couple in each set of experiments as unity, the numbers below express the relative quantities of hydrogen obtained:—

	Water.	Ammonia.	Potash.
A	1	1·8	2·0
B	1	1·75	2·75
C	1	0·91	2·27
D	1	0·36	1·59

from which it appears that the two weakest ammonia solutions augment the action, while the stronger undoubtedly diminish it. The influence of potash is always an accelerating one, but the effect is at the maximum when the alkali is present in comparatively small quantity. These unexpected results were corroborated by the following series of experiments with different strengths of the alkalies.

In I, ammonia, 0·21 per cent. was used; in II, 0·41 per cent.; and in III, 0·78 per cent.

In IV, potash, 0·65 per cent. was used; in V, 1·27 per cent.; and in VI, 2·12 per cent.

Time.	Temperature. Centigrade.	Hydrogen in c.c. reduced to 0° and 760 mm.					
		Ammonia.			Potash.		
		I.	II.	III.	IV.	V.	VI.
4 hours ..	12°	46	36	—	55	60	45
20 „ ..	11·3°	175	128	—	160	175	135
68 „ ..	12°	544	442	—	455	522	416
2 hours ..	14°	75	50	12	36	28	23
18 „ ..	12·5°	358	303	133	205	210	195
66 „ ..	13°	1055	888	861	645	817	743

The ammonia produced in the reaction cannot, it is evident, be the cause of the diminution or of the acceleration already noticed, because where the diminution occurs, the ammonia present would increase the action, and where the increase occurs, it would occasion a decrease. Potash does augment the production of hydrogen, but this throws no light on the cause of the diminution, and only partially accounts for the great amount of reduction at the end of the reaction: for it appears from our experiments that the maximum amount of hydrogen obtainable per day from couples with water corresponding with those used, amounts to 24 milligrams. And leaving out of consideration the influence of the ammonia—which in general is a retarding one—the potash produced in the reaction might give 66 milligrams of hydrogen, whereas the reduction of the last day in Expt. I is equal to 107·2 milligrams above that of the first day, whilst in that of Expt. II it is 185·8 milligrams for the same quantity of couple.

This reduction to nitrite may be shown to an audience as follows:—

Pour a solution of nitre—about 10 per cent.—with enough copper sulphate to colour the liquid distinctly, on to some granulated zinc in a tap-funnel; leave it for a few seconds, and then run off some of the liquid, when the green colour of copper nitrite will be evident. Drop the remainder of the liquid into some starch-solution with potassium iodide and acetic acid: the blue iodide of starch will be instantly formed.

The reaction may also be utilised as a test for nitrates. For this purpose add to about 5 c.c. of solution 12 drops of copper sulphate and four or five pieces of zinc foil ($1 \times \frac{1}{2}$ inch). Wait about three minutes, then pour the liquid, or a part of it, into about 5 c.c. of starch solution containing a little potassium iodide and acetic acid. A blue coloration forms at once, or in a second or two. By inverting the test-tube containing the test before pouring off, the liquid will be seen to

be green. Confirmation may be had by pouring some Nessler reagent into the completely decolorised solution. The reaction with starch can be readily and certainly obtained with 1 part of nitre in 500 of water, and the Nessler reaction with 1 part in 10,000.

Part II.

At least three views may be taken of the foregoing change :—

I. It may be considered that the zinc, augmented in its activity by contact with the copper, combines with the oxygen of the nitrate.

II. That the zinc and copper electrolyse the water present, and that the nascent hydrogen set free effects the reduction in the vicinity of the negative metal.

III. That the two metals electrolyse the nitrate of potassium, with formation of nitrate of zinc, the reduction being effected at the negative pole through the agency of the potassium.

The first view may be expressed by the following equation :—

$$KNO_3 + Zn = ZnO + KNO_2,$$

while the further action requires the intervention of water, with the following result :—

$$KNO_2 + 3Zn + 5H_2O = KHO + 3Zn(HO)_2 + NH_3.$$

Of course this may be brought about by the formation of intermediate compounds.

The second view may be represented thus—

$$(a.)\ Zn \mid OH_2 \mid Cu = ZnO \mid H_2 \mid Cu,$$
$$(b.)\ KNO_3 + H_2 = H_2O + KNO_2,$$
$$(c.)\ KNO_2 + H_6 = H_2O + NH_3 + KHO.$$

And the third view thus—

$$Zn \mid NO_3K \mid NO_3K \mid Cu = Zn(NO_3)_2 \mid K_2 \mid Cu.$$

It may be conceived that this potassium is actually set free and at once acts upon the water, thus—

$$K_2 + 2H_2O = 2KHO + H_2;$$

or other combinations of the elements present may be easily conceived to take place with the same final result.

The KHO and $Zn(NO_3)_2$ produced would of course react, with formation of zinc hydrate and potassium nitrate, so that the several changes at each cycle produce a molecule of hydrogen or its equivalent, which acts on nitre in accordance with equations *b* and *c*.

With reference to the first view, it was found that powdered zinc

and dry nitre, when heated together, detonate explosively, a quantity of gas—probably nitrogen—being produced, together with a solid, consisting of zinc oxide and potassium nitrite and oxide. And Schönbein and Divers have shown that a solution of nitre is reduced by metals more positive than zinc to potassium nitrite and ammonia; but in this case it must be borne in mind that hydrogen is simultaneously produced by the decomposition of water.

Again, an experiment suggested itself which we hoped would assist in deciding between this and the second and third views. A boxwood cell was cut vertically into two equal parts, some pieces of parchment paper were placed between these, and the divisions of the cell held firmly together by a clamp. A solution of nitre was placed in each of the divisions, a strip of zinc being placed in one, a strip of platinum in the other. The strips were connected together by a metallic wire, and allowed to remain so for two or four days, the action being a feeble one. The general result of several experiments was, a little ammonia in each of the divisions; free potassium hydrate in the platinum one, none in the zinc; and about ten times less nitrite in the platinum than in the zinc division.

This great increase of nitrite in the zinc division would appear to lend material aid to the first view, which requires the reduction to take place by, and in the immediate vicinity of, the zinc plate. At this stage it occurred to us that this reduction might, after all, be due to a couple action, the negative element of such couple being the impurities in the zinc itself; and on trial, we found that similar zinc, when not connected with platinum, reduced nitre to almost the same extent as when metallically associated with that metal as described above. Moreover, we found that equal quantities of granulated redistilled zinc and commercial zinc placed in contact with equal volumes of nitre solution gave in equal times nitrite in the ratio 1 : 2·7. No deduction can therefore be drawn from the presence of the proportionately large amount of nitrite in the zinc division of the cell.

That an electric current traverses the nitre solution in the cell experiment, from the zinc to the platinum in the liquid, was ascertained by including a galvanometer in the circuit, which, in conjunction with the appearance of potassium hydrate in appreciable amount along with an excess of unaltered nitre in the platinum division, lends, we think, material aid to hypothesis III.

Whether hypothesis I or III be the more tenable may not be considered yet decided, but the results exhibited in the following table of a series of comparative experiments on the action of the couple on water, and on solutions of potassium nitrate and nitrite, certainly point to the untenability of II.

Employed for No. 1 KNO_2, 500 c.c. of ·922 per cent.
„ „ No. 2 „ 481 „ „ ·956 „
„ „ No. 1 KNO_3, 435 „ „ 1·25 „
„ „ No. 2 „ 462 „ „ 1·18 „

For comparison the total work done by the couples in the given times is expressed in milligrams of hydrogen.

Time in hours.	Water.		KNO_2.		KNO_3.	
	1.	2.	1.	2.	1.	2.
2	2	1·5	40·2	33·8	31·7	34·6
20	20·2	17·2	118	106	106	108
28	29·4	24·4	200	198	124	144
45	46	39	209	211	183	193
93	87	73	273	247	222	239
101	93	84	293	272	No observation	
117	108	96	—	309	234	247
141	132	116	—	—	237	243
148	136	120	—	—	296	—
165	153	134	—	—	331	369

It is evident that the nitre does not simply remain passive, and allow itself to be reduced by the hydrogen evolved from the direct decomposition of water by the couple, which hypothesis II requires: for were this the case, the reduction of the salt, at least at the beginning of the action, would be equivalent only to the hydrogen set free from the water couple alone, whereas the oxygen actually removed is equivalent to about 19 times that amount. It is noticeable that the first numbers given by the nitrite and the nitrate are nearly the same, and that in the respective columns of the salts they do not diverge much from one another for some time, which is of considerable interest, as showing that the ammonia and potassium hydrate, which must pour into the solution in the nitrite experiment from its very commencement, do not materially augment the action of the couple.

The weight of evidence certainly inclines to hypothesis III, which is to a great extent confirmed by the following experiments.

Electrolysis of Nitrate of Potassium.

I. A V-shaped tube was used, the bend being well plugged with fine asbestos. About 25 c.c. of a 5 per cent. solution of nitre were poured into each of the limbs. An amalgamated zinc plate 1·5 centimeters wide, connected by a wire with the platinum end of 4 Grove's cells, was immersed to the depth of one decimeter in one limb of the tube, a copper plate, of double the surface connected with the zinc end of the

battery, being placed in the other. The current was allowed to pass through the liquid for four hours. A trace only of gas escaped from the copper electrode, in the vicinity of which alkali was found immediately after making connection. A quantitative examination of the solutions in the respective limbs gave, in addition to the undecomposed nitre—

Zinc limb	0·3273	grams	$Zn(NO_3)_2$
Copper limb	0·197	,,	KHO
	0·0765	,,	KNO_2
	0·00375	,,	NH_3.

The amount of zinc nitrate was ascertained by precipitating the metal as carbonate, and calculating the oxide subsequently obtained as nitrate. Had zinc oxide been produced in this experiment and passed into solution, this method of analysis would give a quantity of nitrate greater than that actually present. The question therefore arose, does zinc oxide form in the experiment? and, if so, does it dissolve in a solution of nitre or zinc nitrate? We agitated zinc hydrate with nitre solution, also boiled the substances together. No zinc passed into solution. Small quantities of zinc hydrate were agitated with a solution of zinc nitrate. None disappeared. Schindler also states (*Gmelin*, v, 34) that zinc oxide when boiled with the nitrate does not dissolve. Again, zinc oxide was looked for on the zinc plate, and in the solution in its neighbourhood, during the action in this and subsequent experiments. Not a trace could be seen even when 20 Grove cells were employed. Every NH_3, therefore, represents 4 of the $Zn(NO_3)_2$ estimated as described, as seen by the equation :—

(*a*.) $4Zn \mid 8NO_3K \mid Cu = 4Zn(NO_3)_2 \mid K_8 \mid Cu$
(*b*.) $8K + 6H_2O + KNO_3 = 9KHO + NH_3$,

and every KNO_2 represents one of zinc nitrate, thus :—

(*c*.) $Zn \mid 2NO_3K \mid Cu = Zn(NO_3)_2 \mid K_2 \mid Cu$
(*d*.) $K_2 + H_2O + KNO_3 = KNO_2 + 2KHO$.

Calculating then the ammonia and nitrite found in the copper limb into zinc nitrate, according to these equations, we obtain 0·337 gram of that salt, which is 0·01 in excess of that found in the zinc limb by analysis, and equal to 0·0043 gram of zinc oxide—a quantity which might have formed on the zinc plate and yet have escaped detection.

II. A 3 per cent. solution was used in this experiment. In other respects it was similar to the last.

Found in zinc limb.....	0·2596	gram	$Zn(NO_3)_2$
Copper limb	0·1366	,,	KHO
	0·05355	,,	KNO_2
	0·00294	,,	NH_3,

the two latter of which products give 0·2501 gram of $Zn(NO_3)_2$, which is slightly less than that found.

III. A 3 per cent. solution was used, the current passed for three hours. In other respects similar to I and II.

Found in zinc limb	0·1645 gram	$Zn(NO_3)_2$
Found in copper limb	0·0942 ,,	KHO
	0·03706 ,,	KNO_2
	0·00157 ,,	NH_3,

the latter of which are equal to 0·1524 gram of $Zn(NO_3)_2$, which is again below that actually found by analysis. We may therefore conclude, that in these experiments nitre alone suffered electrolytic decomposition.

One other point is worthy of notice here. In the experiments just described not a trace of nitrite or ammonia could be detected in the zinc limb, which we think finally disposes of hypothesis I, because, if the zinc electrode, when charged with positive electricity, fails to reduce nitre in its immediate vicinity, the zinc of the couple so charged might reasonably be expected not to act. Of course we do not contend that in these electrolytic experiments we have identically the same conditions as obtain in the couple decompositions, but that we have a similarity of condition no one can doubt.

Potassium Chlorate.

Action of Couple.—Thorpe (*Chem. Soc. Jour.*, 1873, 547) has shown that our couple reduces potassium chlorate to chloride.* We have studied this reaction with the view of ascertaining whether chlorite or hypochlorite forms during the passage of the salt to chloride. So far as we have been able to determine, these intermediate compounds are not produced. It may be remarked that the chlorate is more rapidly reduced than the nitrate. Thus in a comparative trial, employing equivalent quantities of the two salts, and similar couples, the hydrogen equivalent to the reduction was such as to give the following ratios:—

	Nitrate.		Chlorate.			Nitrate.		Chlorate.
1st hour	1	:	1·15	5th hour		1	:	3·86
3rd ,, ...	1	:	2·50	21st ,, ...		1	:	2·97

Electrolysis.—As soon as an aqueous solution of this salt begins to be

* This reaction may be utilised for the detection of small quantities of chlorates. Add some twelve drops of strong cupric sulphate to about 5 c.c. of solution, then 3 or 4 pieces of zinc foil about 1 inch × ½, boil for a minute or two, or wait till solution is decolorised, filter if necessary and add to the filtrate a few drops of nitric acid and nitrate of silver. A very minute quantity can thus be detected.

electrolysed by an external battery, alkali may at once be detected close to the negative electrode, but instead of the potassium chlorate being reduced to chloride, the greater part of the hydrogen escapes as gas. Employing the arrangement as used for the nitre solution, a current of four cells gave in four hours 0·00244 gram of potassium chloride in the copper limb, and 0·4775 of zinc chlorate in the zinc limb. Calculating the equivalent of the potassium chloride found according to the equations—

$$(a.)\ 3Zn \mid 6ClO_3K \mid Cu = 3Zn(ClO_3)_2 \mid K_6 \mid Cu.$$
$$(b.)\ K_6 + 3H_2O + KClO_3 = 6KHO + KCl.$$

we get only 0·0228 of zinc chlorate. Therefore 95·2 per cent. of the hydrogen formed in the experiment passed through the liquid.

About four years ago it was pointed out by one of us (*Chem. Soc. Jour.*, 1874, p. 415) that finely divided copper, immersed in acidulated water, agglomerated—that is, formed into more or less coherent lumps—when subjected to the action of nascent hydrogen: also that the finely divided particles of palladium and platinum—metals known to condense hydrogen, agglomerated, when similarly treated; further, that the agglomerated copper, palladium, &c., deglomerated when treated with nascent oxygen:—from all which it was inferred that the copper of the couple was also capable in a slight degree of absorbing hydrogen gas.

Graham has shown that occluded hydrogen is a somewhat powerful reducing agent; and to us, having traced the reducing action of the couple in some way to hydrogen, it appeared of exceptional interest to ascertain whether hydrogen associated with the finely divided copper of the couple could reduce nitre to nitrite. With this object some copper was precipitated by immersion of a zinc plate in a 2 per cent. solution of copper sulphate till decolorised. As has been already pointed out, the deposit thus obtained contains metallic zinc. To remove this and to charge the residual metal with hydrogen, dilute sulphuric acid was added, which immediately brought about a powerful agglomeration of the copper. After standing with the acid for about an hour, with occasional shaking, the metal was well washed, and some nitre solution added, when almost immediately the whole deglomerated, shrinking in volume to about a quarter. The solution contained a small quantity of both ammonia and potassium nitrite, which was found equal per 100 grams of copper to 4 milligrams of hydrogen.

For the next trial copper was deposited as before, but from a 1 per cent. solution of the sulphate. The deposit was treated with successive portions of copper sulphate for some hours. The residual metal was then divided into two portions. To one, some nitre solution was added; to the other some dilute sulphuric acid. This after shaking

was poured into a dish, at the bottom of which was a sheet of platinum in connection with the zinc end of 4 Grove's cells. As soon as the metal had settled, the positive electrode was dipped into the acidulated water near its surface. The copper slowly agglomerated without material change in colour, and in about 30 minutes hydrogen was freely escaping from it. After washing this a few times, and neutralising with potassium hydrate, a quantity of nitre was added equal to that added to the first portion. Ammonia and nitrite were found in both. The portion not treated with hydrogen gave, per 100 grams of copper, 3·5 milligrams of hydrogen, the agglomerated giving, for a similar quantity of copper, 8 milligrams of hydrogen. Zinc was also found in small quantity in both, but the non-agglomerated contained at least four times the amount of that present in the hydrogenised. Another effort was made to get the finely divided copper free from zinc. Some deposit, obtained as in the last experiment, was digested, with occasional shaking, for three days with about 5 per cent. solution of copper sulphate. It was then well washed and divided into two parts. To one some nitre was added. The other, previously to the addition of an equal quantity of this salt, was digested with dilute sulphuric acid for an hour, washed, again mixed with dilute acid, hydrogenised for two hours, and the adhering acid neutralised with potash. The non-hydrogenised contained nitrite and ammonia, equal, per 100 grams of copper, to 2·7 milligrams of hydrogen. The hydrogenised portion, for the same amount of copper, contained 19·3 milligrams of hydrogen. Both portions still contained a small quantity of zinc—whether as metal or oxide, or both, there is no means of determining. It is certain that some oxide existed in the portions not treated with acid, and some zinc may have existed as metal, but completely protected by a covering of copper. The reduction effected by the non-hydrogenised portions may also be due to hydrogen occluded during their preparation, but we cannot speak with certainty about it, in consequence of the possible presence of metallic zinc. There can be no doubt, however, that the finely divided copper of our couple does condense hydrogen, and when in this condition reduces nitre to nitrite and ammonia.

Two facts which appeared difficult to reconcile, now appear intelligible enough: the one, that the couple reduces the chlorate in the cold without the least escape of hydrogen; the other, that in the ordinary electrolysis of the chlorate, nearly the whole of this gas escapes without reducing the salt. The reason is obvious. In the first case the hydrogen is probably wholly occluded the moment it is set free, while in the other, only a small quantity of the gas is condensed by the negative plate.

Taking into consideration all the facts brought out by this inquiry, we consider it proved that—

a. The action of the copper-zinc couple on these oxy-salts is of an electrolytic nature.

b. The negative radicle combines with the zinc, whilst the positive radicle, or its equivalent of hydrogen from decomposed water, is set free against the copper crystals.

c. The reduction and hydrogenisation of the salt take place in the immediate vicinity of the negative metal.

We also think it probable that hydrogen is actually set free against the copper, but is condensed by the finely divided metal, and in that condition does its work of reduction and hydrogenisation.

Of course the resulting zinc compound and the alkaline hydrate decompose one another, producing the original salt and zinc hydrate.

Ammonium Nitrate.

It may be assumed that this action of the couple is a general one, true not only of nitre, but of all nitrates containing metals which decompose water at the ordinary temperature. Ammonium nitrate, though not strictly belonging to this class of bodies, should, according to what is known of the electrolysis of ammonium salts, and to the views just enunciated, give off a fourth of the hydrogen in its positive radicle when its solution is subjected to the action of the couple; and since it is very probable that the real reducer in these actions is hydrogen, it naturally occurred to us that this salt ought not to form an exception to the above generalisation. But to place the matter beyond doubt, we instituted a few additional experiments.

A qualitative experiment with the couple showed at once that both nitrite and ammonia were produced, but not hyponitrite.

We give the details of a quantitative trial:—410 c.c. of about 1·2 per cent. solution of ammonium nitrate were added to the usual quantity of couple (temp. 15° C.), and the ammonia and nitrate estimated. Subjoined are the results reckoned for 100 parts of solution:—

Time.	NH_3.	NH_4NO_2.	Equivalent to NH_4NO_3.	Work done each hour expressed in milligrams of Hydrogen.
1 hour.....	0·039	0·209	0·4445	100
4 hours	0·114	0·185	0·767	45·5
11 „	0·179	0·159	1·04	16·4
23 „	0·243	Nil	1·143	7·8

The action of heat on a solution of ammonium nitrite resolves it, as is well known, into nitrogen and water, from which it was inferred

that were this reduction attempted at or near the boiling point of the solution of the nitrate, the nitrite as quickly as produced would be decomposed in like manner. On trial, gas was evolved, but this proved to be mainly nitric oxide, which gas Thorpe had noticed on boiling solution of ammonium nitrate with the couple (*Chem. Soc. Journal*, 1873, p. 544). The amount of this oxide of nitrogen we found increased with the strength of the nitrate solution. Thus with strengths of 20, 10 and 5 per cent. and an excess of couple, the nitric oxide was 8·5, 6 and 3 respectively. In the cold the nitrate, even in solution of 20 per cent., was completely reduced to ammonia in about 24 hours without the escape of nitrogen free or combined. We might suggest therefore that, in estimating unknown nitrates by Thorpe's process, it would be well to allow the couple to remain in contact with the nitrate solution for at least 24 hours prior to distillation.

XIX. *The Alkaloïds of the Aconites.* Part II. *On the Alkaloïds contained in Aconitum Ferox.*

By C. R. Alder Wright, D.Sc., Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry, in St. Mary's Hospital Medical School.

§ 1. *Composition of Pseudaconitine.*

For some years it has been known that the mixtures of alkaloïds extracted commercially from *A. Napellus* and *A. ferox* are not at all identical, and it has been shown by von Schroff, T. B. Groves, and others, that the approximately pure alkaloïds isolated from the two species, and purified by crystallisation from ether, alcohol, &c., differ in this respect, that whilst the *Napellus* base yields well crystallised salts with facility, that from *A. ferox* does not form any kind of crystallisable salt at all (as shown below, we have found that there are exceptions to this rule). Accordingly, the terms aconitine and pseudaconitine have been employed to designate the two alkaloïds. These two substances have probably been confused together by most of the older experimenters on the aconite alkaloïds, who moreover did not obtain the crystallisable bases free from uncrystallisable alkaloïds accompanying them (or formed from them by decomposition during extraction ?).

The results detailed in Part I of these researches (this *Journal*, 1877, i, 143) tend to show that the crystallisable physiologically active base

of *A. Napellus* is a uniform homogeneous alkaloïd indicated, when perfectly pure (to obtain which condition is a matter of some difficulty), by the formula $C_{33}H_{43}NO_{12}$; for the perfectly pure base isolated from several specimens of roots exhibited exactly the same properties, and gave identical numbers agreeing well with this formula. Further experiments, which will be given in detail in a future paper, show that under certain conditions this base readily loses the elements of water, forming a well crystallised anhydro-derivative, closely resembling the parent base; the somewhat irregular numbers obtained with different specimens of aconitine nearly, but not perfectly purified, are probably in many cases due to varying admixture of this derivative (produced during the process of extraction) with the unaltered aconitine. When subjected to the action of saponifying agents, it breaks up in accordance with the equation—

$$C_{33}H_{43}NO_{12} + H_2O = C_7H_6O_2 + C_{26}H_{39}NO_{11},$$

forming *benzoic acid* and a new alkaloïd. The crystallisable physiologically active base of *A. ferox* is in many respects very similar to aconitine. Like that base, it forms a derivative closely resembling the parent alkaloïd, by loss of the elements of water; and the presence of this derivative, formed during the process of extraction, in the base obtained from the roots can, under certain conditions, be recognised: the action of saponifying agents, however, sharply distinguishes the *A. ferox* base, pseudaconitine, from the aconitine of *A. Napellus:* for it splits up, by a reaction parallel to the above, forming an acid identified as *dimethylprotocatechuic acid*, $C_6H_3\begin{cases}COOH\\O.CH_3\\OCH_3\end{cases}$, together with a new alkaloïd altogether different from that produced in like manner from aconitine.

In Part I it was incidentally stated that pseudaconitine is represented by the formula $C_{36}H_{49}NO_{11}$: since these earlier experiments were made, we have found that the base then examined was not wholly pure, as it contained an admixture of the anhydro-derivative, *apopseudaconitine*, above referred to: pseudaconitine, when perfectly pure, is represented by the formula, $C_{36}H_{49}NO_{12}$, apopseudaconitine being formed from it by the reaction,

$$C_{36}H_{49}NO_{12} = H_2O + C_{36}H_{47}NO_{11}.$$

The specimen of alkaloïd from which these earlier results were obtained was prepared by Mr. T. B. Groves (*Year-book of Pharmacy*, 1873, 500) by exhausting the powdered roots with methylated spirit acidulated with hydrochloric acid in the proportions of 2 drachms to the gallon (1 in 640 by volume, corresponding to about 0·06 per cent. by

weight of anhydrous HCl), evaporating to a small bulk, and extracting alkaloïds by means of ammonia and ether, the ethereal solution being allowed to evaporate spontaneously, and the crystals thus formed separated from noncrystalline matter by filtration, pressure and crystallisation from alcohol. Owing to accidental circumstances, however, some six or seven weeks elapsed between the concentration of the alcoholic extract to a small bulk and the further treatment of the concentrated liquid; probably this circumstance (or perhaps some overheating during evaporation, &c.) was the cause of the partial dehydration of the pseudaconitine; for other batches of roots worked up by Messrs. Hopkin and Williams (with the sole difference that 30 grains of strong sulphuric acid were used per gallon of alcohol instead of 120 of aqueous hydrochloric acid, which is not far from the same proportion of actual anhydrous acid) yielded, as described below, an alkaloïd which had not been noticeably dehydrated at all; whilst the results detailed in § 4 show that contact with excess of dilute hydrochloric acid at 100° for some hours suffices entirely to convert pseudaconitine into apopseudaconitine. The following numbers were obtained:—

(A). Crystallised base as received from Mr. Groves dissolved in a mixture of alcohol and ether, and recovered by spontaneous evaporation:—

0·3165 gram dried at 100° gave 0·7410 CO_2 and 0·2180 H_2O.
0·8090 gram gold-salt gave 0·1575 Au.

(B). Second crop of crystals regained from mother-liquors of A by further spontaneous evaporation:—

0·2925 gram dried at 100° gave 0·6805 CO_2 and 0·1970 H_2O.
1·3260 gram gold-salt gave 0·2565 Au.
0·5730 gram of base burnt with soda-lime gave 0·0845 Pt.

	Calculated for		Found.	
	$C_{36}H_{49}NO_{12}$.	$C_{36}H_{47}NO_{11}$.	A.	B.
Carbon in base....	62·88	64·58	63·84	63·45
Hydrogen „	7·13	7·03	7·65	7·48
Nitrogen „	2·04	2·09	—	2·09
Gold in gold-salt ..	19·10	19·44	19·46	19·34

Manifestly these numbers agree well with mixtures of pseudaconitine and apopseudaconitine, the latter being contained in larger proportion in Specimen A, as might be expected from its somewhat less solubility in alcohol and ether (*vide* § 4).

Another sample of pseudaconitine prepared by Mr. Groves from a different batch of roots, and purified not only by numerous crystallisations, but also by conversion into mercuriodide and regeneration

therefrom, gave numbers closely accordant with the formula $C_{36}H_{49}NO_{12}$—

0·3540 gram gave 0·8140 CO_2, and 0·2410 H_2O.
0·3195 gram gave 0·7365 CO_2, and 0·2200 H_2O.

	Calculated for $C_{36}H_{49}NO_{12}$.	Found.	
Carbon	62·88	62·71	62·87
Hydrogen.....	7·13	7·57	7·65

Unfortunately this specimen was too small in quantity for any extended examination.

In order to subject pseudaconitine to a thorough examination several ounces were purchased of the rough alkaloïd extracted from *A. ferox* roots by Messrs. Hopkin and Williams by percolation with alcohol acidulated with sulphuric acid in the proportion of 30 grains to the gallon (about 0·05 per cent. by weight); from this the crystallised base was prepared by dissolving in ether, filtering from a little undissolved matter, and allowing to evaporate spontaneously after admixture with about half its bulk of "light petroleum distillate" (that portion of the "benzoline" of the oil-shops which distilled off in a water-bath). A large crop of crystals mixed with a little resinous matter was thus obtained, from which the crystals were separated by stirring up with a little alcohol (which dissolved the resinous matter with some of the crystals) and filter-pumping. These crystals were again crystallised from ether-petroleum, furnishing a crop of apparently homogeneous crystals (1). To see whether these consisted of the pure base they were purified by solution in hot alcohol, addition of hot water till a milkiness appeared, clearing up by addition of a few drops of alcohol, and slow cooling; white cauliflower-like crystals thus formed (2). Another portion of crystals (1) were crystallised four times more from ether-petroleum (3). From these three specimens the following numbers were obtained:—

Specimen (1). 0·3225 gram gave 0·7465 CO_2 and 0·2135 H_2O.
0·3840 gram gold-salt gave 0·0750 Au.
Specimen (2). 0·2395 gram gave 0·5540 CO_2 and 0·1610 H_2O.
0·5105 gram burnt with soda-lime gave 0·0765 Pt.
0·7045 gold-salt gave 0·1385 Au.
Specimen (3). 0·2380 gram gave 0·5460 CO_2 and 0·1580 H_2O.
0·3025 gram gold-salt gave 0·0590 Au.

	Calculated for $C_{36}H_{49}NO_{12}$.	Found. (1.)	(2.)	(3.)
Carbon.....	62·88	63·11	63·09	62·57
Hydrogen	7·13	7·36	7·47	7·37
Nitrogen.....	2·04	—	2·12	—
Gold in Au-salt	19·10	19·53	19·66	19·50

It is evident from these numbers that the crystallised base thus obtained was essentially pseudaconitine, but the high percentage of gold found in the gold-salt seems to indicate that (just as with aconitine, Part I), mere crystallisation of the free base from ether, alcohol, &c., does not suffice to free it entirely from accompanying substances; a circumstance clearly proved by the following numbers obtained with base purified by conversion into recrystallised nitrate, regeneration, and crystallisation from ether-petroleum.

Specimen A.—Nitrate prepared from the crude material supplied by Messrs. Hopkin and Williams; crystals of the salt were prepared by rubbing in a mortar the rough alkaloïd with enough dilute nitric acid to dissolve it, adding a few drops of concentrated nitric acid, and vigorously rubbing for some time, whereby a thick magma of crystals was formed; this was drained on the filter-pump, washed with weak nitric acid, dissolved in warm water, and made to crystallise again by addition of a few drops of concentrated nitric acid, and stirring. The crystals thus obtained were perfectly white after filter-pumping and washing with dilute nitric acid; they were again crystallised in the same way, and then decomposed by dissolving in water, adding sodium carbonate and shaking with ether; the base which crystallised from the ether on spontaneous evaporation was washed with a little alcohol on the pump-filter, and then constituted a snow-white crystalline mass:—

0·2775 gram dried at 100° gave 0·6400 CO_2 and 0·1845 H_2O.

0·2920 gram dried in a current of air at 80° gave 0·6700 CO_2 and 0·1980 H_2O.

0·5015 gram gold-salt gave 0·0970 Au.

Specimen B.—Similarly prepared, the purified alkaloïd recrystallised from ether and petroleum several times (Specimen 3, *supra*) being employed in the first instance instead of the impure base obtained from Messrs. Hopkin and Williams.

0·2880 gram dried at 100° gave 0·6610 CO_2 and 0·1920 H_2O.

0·5655 gram gold-salt gave 0·1085 Au.

0·3090 gold-salt gave 0·0592 Au.

0·0230 gram of base dried at 100° gave by vacuum-combustion process 0·000473 gram nitrogen.

Specimen C.—The preceding sample of base, B, again converted into nitrate, recrystallised, and regenerated from the salt:—

0·2750 gram dried at 100° gave 0·1845 H_2O and 0·6330 CO_2.

0·4640 gram burnt with soda-lime gave by titration of the evolved ammonia 0·00945 gram N; by conversion into platinum salt, 0·0695 Pt.

0·5550 gram gold-salt gave 0·1070 Au.

University of Michigan

	Calculated.		Found. A.		B.	C.		Mean.
C_{36}	432	62·88	62·90	62·57	62·59	62·77		62·71
H_{49}	49	7·13	7·39	7·53	7·41	7·45		7·44
N.....	14	2·04	—	—	2·06	2·03	2·12	2·07
O_{12}	192	27·95	—	—	—	—	—	—
$C_{36}H_{49}NO_{12}$	687	100·00						

Calculated for $C_{36}H_{49}NO_{12},HCl,AuCl_3$.	A.	Found. B.		C.	Mean.
Gold = 19·10	19·34	19·18	19·16	19·28	19·24

The determination of the nitrogen in B was made by combustion with oxide of copper and metallic copper in a Sprengel vacuum. 0·0230 gram of base thus gave 27·95 c.c. of CO_2, and 0·377 of N at 0° and 760 mm. (corrected by subtracting the minute amounts of each gas obtained in a blank experiment made simultaneously), or 0·0150 gram carbon, and 0·000473 of nitrogen. These values give 65·2 per cent. of carbon, somewhat too high, but not more so than the experimental errors might account for; the volume ratio of N to CO_2 is $\frac{0·377}{27·95} = \frac{1}{74·2}$, giving the "atom"- ratio $\frac{1}{37·1}$, the calculated ratio being $\frac{1}{36}$.

Pseudaconitine is far more readily soluble in alcohol and ether than aconitine; when crystallised from ether, or, better, ether and petroleum spirit, it forms transparent needles and sandy crystals; but if the evaporation be not extremely slow, and especially from alcoholic solutions, it is apt to separate as a varnish at the upper edge of the solution, soon becoming a confused mass of milk-white cauliflower-like crystalline efflorescence: the crystals, when air-dry, are hydrated, the water of crystallisation being lost at 80° in a current of dry air without any fusion or fritting; if heated to 100°, the hydrated crystals lose their water with fritting more or less marked (the anhydrous base also frits at 100°, but less quickly).

Crystals from Specimen No. 3 of base purified by several crystallisations from ether-petroleum; 0·6640 gram of air-dry crystals lost at 100° 0·0175..... = 2·65 per cent.

Crystals from base purified by conversion into nitrate and regeneration (Specimen A *supra*); 1·2770 gram lost at 80° in a current of dry air 0·0360 ..... = 2·82 „

Base from nitrate (Specimen C *supra*); 1·0020 gram lost at 100° 0·0270 ..... = 2·69 per cent.

Calculated for $C_{36}H_{49}NO_{12},H_2O$..... = 2·55 „

The salts of pseudaconitine, for the most part, are so extremely difficult to crystallise that hitherto they have only been obtained as varnishes by spontaneous evaporation; the kind of treatment above described, which yielded a crystallised nitrate, did not answer with the sulphate, hydrochloride, acetate, oxalate, &c. If the alkaloïd be dissolved in just sufficient dilute warm nitric acid to form a nearly neutral salt, the liquid generally dries up to a varnish without crystallising; if, however, a crystal of nitrate be placed in the liquid and the whole well stirred, the dissolved salt gradually separates in crystals: crystallisation takes place, however, with far greater facility on adding a few drops of concentrated nitric acid and stirring vigorously. The following numbers were obtained with a specimen of the salt recrystallised from a nearly neutral aqueous liquid:—

0·7920 gram of air-dry salt lost at 100° 0·0570 = 7·19 per cent.
Calculated for $C_{36}H_{49}NO_{12},HNO_3,3H_2O$ = 6·72 „
0·2680 gram of dry substance gave 0·5740 CO_2 and 0·1805 H_2O.

	Calculated.	Found.
Carbon	57·60	58·39
Hydrogen	6·67	7·48

The condensed water was strongly acid, as might have been expected in the combustion of a nitrate; whence also the high value for the carbon found.

The gold-salt of pseudaconitine is distinctly crystalline when precipitated from a dilute solution: after drying over sulphuric acid it can be readily crystallised from boiling alcohol in minute needles only sparingly soluble in cold alcohol: when air-dry the crystals are anhydrous. The following combustions of different specimens of gold-salt were made, the high percentage of carbon found being apparently due to the escape of a minute quantity of chlorine liberated on heating the gold-salt; for the condensed water contained chlorine, and strongly acted on iodide and starch-paper.

(A) Gold-salt prepared from base only purified by repeated crystallisation from ether-petroleum—
0·3215 gram gave 0·5025 CO_2 and 0·1545 H_2O.

(B) Another sample similarly prepared—
0·2930 gram gave 0·4600 CO_2 and 0·1410 H_2O.

(C) Prepared from base regenerated from nitrate—
0·4660 gram gave 0·7280 CO_2 and 0·2205 H_2O.

(D) Another specimen similarly prepared—
0·3250 gram gave 0·5125 CO_2 and 0·1560 H_2O.

	Calculated for $C_{36}H_{49}NO_{12},HCl,AuCl_3$.	Found. A.	B.	C.	D.
Carbon	42·11	42·61	42·82	42·60	42·99
Hydrogen ..	4·87	5·34	5·35	5·25	5·33

Although crystallisable, the auro-chloride does not seem to be as well suited for the final purification of the nearly pure base as is the nitrate; a sample of salt prepared from the nearly pure base crystallised several times from ether-petroleum (Specimen (3) *supra*), and containing originally 19·50 per cent. of gold was recrystallised from boiling alcohol: the crystals dried over sulphuric acid and finally at 100° were not perceptibly altered; 0·8095 gram gave 0·1575 Au = 19·47 per cent. On the other hand, as above stated, when the same sample of base was converted into nitrate, recrystallised, and the base regenerated, the gold-salt finally obtained contained 19·18 and 19·16 per cent. Au (Specimen B, *supra*), the theoretical value being 19·10. It is noteworthy that just the same thing is observable with aconitine, no diminution in percentage of gold being noticeable on crystallising from alcohol the gold-salt (prepared from the alkaloïd crystallised from ether, &c., only), whilst as shown in Part I, a diminution of 0·2 to 0·3 per cent. is brought about by conversion into hydrobromide and recrystallising and regenerating the base, the pure alkaloïd thus obtained furnishing a gold-salt containing the theoretical percentage of gold, whilst the original approximately pure base contained too high an amount by 0·2 to 0·3 per cent.

The mercuriodide of pseudaconitine prepared by precipitating a solution of the base in acetic acid by potassium mercuriodide, is an amorphous, flocculent, white precipitate, very sparingly soluble in water: after washing and drying at 100°—

0·5510 gram gave 0·2970 AgI	Iodine = 29·12 per cent.
Calculated for $C_{36}H_{49}NO_{12},HI,HgI_2$	,, = 30·02 ,,

Pseudaconitine is sparingly soluble in water and in fixed caustic alkalis, somewhat more readily in ammonia and sodium carbonate; from the latter solution, if saturated, it can be regained in an impure state (owing to incipient saponification) by quickly evaporating, when the alkaloïd separates as a resinous film which yields crystals on solution in ether, addition of petroleum spirit, and spontaneous evaporation, if it have not been too long exposed to the action of the hot alkaline fluid. In its qualitative reactions it closely resembles aconi-

tine, being precipitated by mercuric chloride (precipitate redissolved on moderately large dilution); potassium mercurobromide (precipitate only sparingly soluble on adding water); potassium mercuriodide (precipitate very sparingly soluble); tannin; iodine dissolved in potassium iodide; gold chloride; caustic potash, soda, and ammonia; sodium carbonate, &c.; the precipitates being more or less readily dissolved on largely diluting with water. Platinic chloride only forms a precipitate in concentrated solutions, the salt being pretty readily soluble in water and also in alcohol. From aconitine pseudaconitine differs sharply in molecular weight, and in solubility in alcohol and ether; also in crystallising with H_2O (aconitine crystallises anhydrous, Part I); and more especially in melting point: as stated above pseudaconitine slightly frits at 100°; in a capillary tube it melts to an extremely viscid, transparent fluid at about 104—105°, the exact point of fusion not being very distinctly marked; whilst pure aconitine first melts completely at 189° (corrected), a slight fritting and browning being noticeable a few degrees below the melting point. As shown below, the action of saponifying agents on pseudaconitine gives rise to dimethyl protocatechuic acid; whilst under the same conditions, as will be shown in a future paper, aconitine gives rise to benzoic acid.

Pseudaconitine can be heated to 105° for some hours without materially darkening in colour or losing in weight (if deprived of its water of crystallisation previously): at somewhat higher temperatures, however, it turns yellowish, and then brownish, and finally dark chestnut, losing in weight several per cents. The loss of weight, however, appears to be due, at least in part, to the removal of substances other than water, as the increase in carbon percentage does not correspond to that due to the loss of weight, assuming water only to be removed: thus, after four hours' heating to 135°, 8·38 per cent. in weight was lost, but the chestnut-coloured varnish produced contained carbon 64·30, hydrogen 7·22; had the 8·38 per cent. lost been due to the removal of water only, the percentages should have been—carbon, 68·63; hydrogen, 6·77. The varnish, when dissolved in tartaric acid and precipitated by sodium carbonate, yielded a base soluble in ether with brown flakes not dissolved by that menstruum; the ethereal solution furnished, by spontaneous evaporation, only a nearly colourless varnish from which no crystals or crystallised salts could be obtained: this amorphous alkaloïd contained carbon, 65·51; hydrogen, 7·50, whilst the composition, $2C_{36}H_{49}NO_{12}—3H_2O$, would require—carbon, 65·45; hydrogen, 6·97. A precisely similar substance was obtained in an experiment made with a view to see if pseudaconitine resembles quinine and cinchonine in the formation of an isomeride by heating the acetate: acetate of pseudaconitine was heated to 130—140° for an hour, and the somewhat coloured mass dissolved in aqueous tartaric

acid and treated with sodium carbonate and ether: the residue left on spontaneous evaporation of the ethereal solution would not yield crystals nor crystalline salts; it contained carbon, 66·27; hydrogen, 8·27, the composition, $C_{36}H_{49}NO_{12}—2H_2O$, requiring—carbon, 66·36; hydrogen, 6·91.

§ 2. *Action of Alkalis on Pseudaconitine.*

When pseudaconitine is heated to 100° in sealed tubes with alcoholic soda for 12 hours or more, it becomes completely broken up, with assimilation of the elements of water, into *dimethyl protocatechuic acid* and a new base, to which it is proposed to apply the term *Pseudaconine*; thus—

$$C_{36}H_{49}NO_{12} + H_2O = C_9H_{10}O_4 + C_{27}H_{41}NO_9.$$

A small quantity of a yellowish resinous bye-product of feebly acid character is also formed by the further action of the alkali on the pseudaconine, but the amount of colouring-matter produced is but small. If, instead of allowing the reaction to take place in a sealed tube, a boiling alcoholic solution of soda be employed, an inverted condenser being attached, complete saponification is also brought about in less than 24 hours, but the amount of resinous bye-product is increased; on the other hand it is diminished if, in the sealed tube, the air be displaced by coal-gas before closing the tube. Thus the following values were obtained, the dimethyl protocatechuic acid formed being extracted by evaporating off the alcohol from the product of the reaction, and treating the residue with hydrochloric acid and ether; three agitations of the acidified aqueous fluid with about its own bulk of ether were found to remove completely the dimethyl protocatechuic acid, which was obtained in a weighable form by simply allowing the ethereal extract to evaporate spontaneously and drying the residue at 100°. As the residue thus obtained contained small quantities of feebly acid resinous amber-coloured bye-product, its alkali-saturating power was carefully determined with decinormal soda solution: the percentages of acid calculated from the weight of the residue and from the soda neutralised in three experiments were as follows:—

(A) 1·0720 gram of pure anhydrous pseudaconitine heated to 100° for 24 hours with alcoholic soda in a tube from which the air had been displaced by coal-gas before sealing up. Residue dried at 100°, weighed 0·3060 gram: soda solution neutralised corresponded to 0·2917 gram of the monobasic acid, $C_9H_{10}O_4$.

(B) 1·3105 gram similarly treated, save that the air was not displaced by coal-gas. Residue weighed 0·3860; soda solution neutralised was equivalent to 0·3733 gram $C_9H_{10}O_4$.

(C) 1·3730 gram boiled with alcoholic soda 24 hours. Residue weighed 0·4440 gram: soda neutralised was equivalent to 0·4372 gram $C_9H_{10}O_4$.

	Calculated for above equation.	Found. A.	Found. B.	Found. C.
Percentage of $C_9H_{10}O_4$ obtained from $C_{36}H_{49}NO_{12}$	26·49			
From weight of residue		28·54	29·45	32·34
From result of titration		27·21	28·48	31·84

The coloured resinous feebly acid bye-product was present in sensibly larger quantity in B than in A, and to a considerably larger amount still in C: whence it is evident that the amounts of pure dimethyl protocatechuic acid actually formed in these experiments were very close to the theoretical quantity, the higher numbers obtained above being manifestly due to the increasing amount of this bye-product. The complementary product, $C_{27}H_{41}NO_9$, pseudaconine, formed in these three experiments, did not contain any undecomposed pseudaconitine, as on subjecting it to a second saponification no dimethyl protocatechuic acid at all was formed, although the resinous bye-product was produced in small quantity.

The dimethyl protocatechuic acid thus obtained dissolved in boiling water, leaving behind a minute amount of resinous matter; on cooling it crystallised out in anhydrous needles. After recrystallisation from boiling water two different specimens (one derived from Mr. Grove's batch of alkaloïd (§ 1), and the other from Messrs. Hopkin and Williams' batch) melted respectively at 176—177° and 177—178° (corrected). On fusion with caustic potash at 250°, acidifying the "melt," and shaking with ether, protocatechuic acid was abundantly formed, easily identified by its peculiar colour-reactions with ferric chloride, &c. On analysis the following numbers were obtained:—

0·2325 gram gave 0·5030 CO_2 and 0·1175 H_2O.

	Calculated.		Found.
C_9	108	59·34	59·01
H_{10}	10	5·49	5·62
O_4	64	35·17	—
$C_9H_{10}O_4$	182	100·00	

The melting point, physical properties, and qualitative reactions (especially the formation of a gelatinous silver-salt on the addition of silver nitrate to the neutral ammonia-salt) of this substance exactly agreed with synthetically prepared dimethyl protocatechuic acid; Beckett and Alder-Wright, however, found (this *Journal*, 1876, i,

304) that the latter crystallised with H_2O: on the other hand, Koelle describes synthetically prepared dimethyl-protocatechuic acid as anhydrous (*Liebig's Annalen*, clix, 240), as is also that prepared by the oxidation of methyl-eugenol (Graebe and Borgmann, *ibid.*, clviii, 282); the acid from pseudaconitine crystallised anhydrous both from boiling water and from ether containing water.*

Attempts yet further to identify this acid as dimethyl protocatechuic acid by distilling it with soda-lime led to but little result on account of the minute yield: Koelle obtained (*loc. cit.*) dimethyl-pyrocatechin (in an impure state) by the reaction—

$$C_6H_3\begin{cases}CO.OH\\O.CH_3\\O.CH_3\end{cases} = CO_2 + C_6H_4\begin{cases}O.CH_3\\O.CH_3,\end{cases}$$

the yield being not more than 5 per cent.: we obtained a small quantity of an oil resembling in appearance and odour the dimethyl pyrocatechin obtained from hemipinic acid by similar treatment (Beckett and Alder-Wright, this *Journal*, 1876, i, 281); the quantity was too small to determine the boiling point, or to purify for combustion, but, on heating with amorphous phosphorus and hydriodic acid to 100° for some time and shaking with ether, a substance was dissolved out readily soluble in water, and giving with ferric chloride the colour reaction of pyrocatechin: the original oily matter did not do this, so that there can be no doubt that the oily body really was dimethyl pyrocatechin converted into pyrocatechin by the hydriodic acid as shown by Beckett and Alder-Wright (*loc. cit.*), thus:—

$$C_6H_4\begin{cases}O.CH_3\\O.CH_3\end{cases} + 2HI = 2CH_3I + C_6H_4\begin{cases}OH\\OH.\end{cases}$$

It is noteworthy that the mixture of pseudaconitine and apopseudaconitine, crystallised from alcohol, and nearly but not quite pure, prepared by Mr. Groves (§ 1), and also the crude alkaloïdal mixture, manufactured by Messrs. Hopkin and Williams, furnished on saponification an acid, from which minute amounts of *benzoic acid* were separable by distillation with a large bulk of water, dimethyl-protocatechuic acid not being thus carried over. By neutralising the distillate with soda, evaporating to a small bulk, acidifying, and shaking with ether, small quantities of benzoic acid were obtained, melting at 120—121° in each instance. The pseudaconitine regenerated from

* Since this paragraph was written it has been shown by Kaeta Ukimori Matsmoto (*Deut. Chem. Ges. Ber.*, xi, 122) that dimethylprotocatechuic acid crystallises anhydrous from hot solutions when the crystals form at a temperature above 50°, and with H_2O from dilute solutions below 50°.

the nitrate, after recrystallisation of that salt, however, did not furnish sensible quantities of benzoic acid by this mode of treatment. It has been stated above, and will be demonstrated in a future paper, that benzoic acid is a product of the saponification of aconitine, whence it appears extremely probable that these two preparations contained small quantities of aconitine, removed by conversion into nitrate, and recrystallising. The amount of aconitine (if aconitine it were) thus present represented only about 0·5 per cent. of the total alkaloïds in the case of the first substance, and 1 per cent. in the case of the second. Whether the base furnishing benzoic acid is a natural constituent of *A. ferox*, or whether it arose in the present instances from admixture of a few roots of *A. Napellus*, or some other species containing aconitine, with the *A. ferox* roots, cannot be determined; this latter is extremely probable, although the former is also very likely, the more so as we have found that the rough alkaloïdal matters obtained from the roots sold as *A. Napellus* furnish a little dimethylprotocatechuic acid on saponification along with much benzoic acid.

Pseudaconine is obtainable in a state of considerable purity by rendering alkaline with sodium carbonate, and evaporating to dryness on the water-bath, the acid liquid obtained by saponifying pure pseudaconitine with alcoholic soda, and removing the dimethylprotocatechuic acid and resinous bye-product formed by shaking with ether. From the residue alcohol dissolves out pseudaconine, which can be purified by evaporating off the alcohol from the clear filtrate, and dissolving the residue in ether, in which it is readily soluble. On spontaneous evaporation a clear, slightly yellow varnish, fusible in the water-bath, is obtained, pretty readily soluble in water, forming a solution of strongly alkaline reaction and bitter taste, *not producing the slightest lip tingling*. The following numbers were obtained with the varnish dried at 100°, till constant in weight:—

0·2970 gram gave 0·2105 H_2O and 0·6680 CO_2.
0·2510 gram gave 0·1795 H_2O and 0·5630 CO_2.
0·9645 gram burnt with soda-lime gave by titration of the evolved ammonia 0·02533 gram N.

	Calculated.		Found.	
C_{27}	324	61·95	61·34	61·17
H_{41}	41	7·84	7·87	7·94
N.....	14	2·67	2·62	
O_9	144	27·54	—	
$C_{27}H_{41}NO_9$	523	100·00		

As yet it has not been found practicable to obtain pseudaconine

in a crystallised state in any quantity; but if a thin film of the base be left on a watch-glass by evaporation of its ethereal solution, and set aside for some weeks, it gradually becomes converted into a mass of well defined acicular crystals a quarter of an inch in length. None of its salts have yet been obtained crystallised.

Unlike pseudaconitine, pseudaconine can be heated to 120—130° for two hours, without losing in weight more than traces; it darkens in colour somewhat by the treatment, however. At higher temperatures it probably loses water, forming an anhydro-derivative (*vide* § 3). The aqueous solution throws down a brown precipitate of silver hydrate from the nitrate, becoming black, and evidently reduced on heating; it reduces ammoniacal silver nitrate on boiling, and gold chloride in the cold on standing, but produces no appreciable reduction of cuprous oxide from Fehling's solution, even when boiled therewith for some time. It readily neutralises acids, requiring quantities of titrated solutions, corresponding to the equivalent 523; the salts have as yet not been obtained otherwise than as varnishes, or scale-preparations. The hydrochloride throws down from gold chloride a yellow precipitate, which either decomposes whilst washing and drying, or else contains reduced gold, as it exhibits no constant composition. Three different specimens contained 23·65, 25·41, and 25·85 per cent. of gold respectively, the formula, $C_{27}H_{41}NO_9,HCl,AuCl_3$, requiring 22·74 per cent.; an aqueous solution of the gold-salt deposited reduced gold on standing over sulphuric acid in the dark.

As a check on the molecular weight, the mercuriodide was prepared by dissolving the base in acetic acid, and adding potassium mercuriodide; it formed a white, amorphous precipitate, of which, after washing and drying over sulphuric acid, and finally at 100°, 0·7240 gram gave 0·4650 AgI, and 0·1540 HgS.

	Calculated for $C_{27}H_{41},NO_9,HI,HgI_2$.	Found.
Iodine	34·48	34·71
Mercury.....	18·10	18·31

In most of its qualitative reactions pseudaconine resembles pseudaconitine, the precipitates being usually somewhat more soluble in water. Caustic potash in excess precipitates it from moderately concentrated solutions, but not from dilute ones. Sodium carbonate does not precipitate saving from the most concentrated solutions, *e.g.*, when a solution in excess of sodium carbonate is evaporated down until the salt begins to crystallise out; the base then partially separates as a fluid mass.

§ 3. *Action of Saponifying Agents on Pseudaconitine at Temperatures above* 100°.

If the saponification of pseudaconitine with alcoholic soda be carried out at a temperature of about 140°, the ultimate products formed differ from those produced at 100°, in this respect, that the base complementary to dimethylprotocatechuic acid contains the elements of H_2O less than pseudaconine, and may therefore be termed *apopseudaconine*. In all probability this is formed by the removal of water from pseudaconitine, forming apopseudaconitine (§ 4), and the subsequent saponification of the base thus produced.

$$C_{36}H_{49}NO_{12} = H_2O + C_{36}H_{47}NO_{11}$$
$$C_{36}H_{47}NO_{11} + H_2O = C_9H_{10}O_4 + C_{27}H_{39}NO_8,$$

and not by the direct dehydration of pseudaconine; for, as above stated (§ 2), pseudaconine is not perceptibly altered by heating to a temperature of about 130°, whilst pseudaconitine loses the elements of water at a temperature considerably below this.

In general and physical properties apopseudaconine closely resembles pseudaconine, the only noticeable difference between them being the numbers given on combustion; no marked increase in the amount of colouring matter and resinous bye-product appears to accompany the employment of the higher temperature for saponification; on the other hand, if water alone be employed instead of alcoholic soda, saponification is brought about at 140°, though not so rapidly as with the alkali, only about 85 per cent. of the pseudaconitine being decomposed in 24 hours; the dimethylprotocatechuic acid thus produced is, however, almost perfectly free from the colouring matter and resinous bye-product formed to a greater or lesser extent when alcoholic soda is used. Thus in two experiments, 22·15 and 22·8 per cent. of dimethylprotocatechuic acid were found (calculated, 26·49) after 24 hours' digestion at about 140°; the alkaloïd extracted from the product of the reaction, when obtained as a varnish by the evaporation of its ethereal solution, and digested with water, did not wholly dissolve, but left behind solid particles of altered pseudaconitine, which furnished dimethylprotocatechuic acid on further saponification; on first moistening the resinous mass with water, it became white and opaque on the surface, and presented the appearance (to the naked eye, not under the microscope) of a crystalline film; this appearance is not presented by pure apopseudaconine, freed from all traces of substances capable of saponification (pseudaconitine and the products of the action of heat thereon) by the action of alcoholic alkali. In a preliminary report to the Pharma-

ceutical Conference (*Year-book of Pharmacy*, 1877, 444), this appearance was erroneously supposed to be characteristic of pseudaconine, which was then confounded with apopseudaconine, the exact formula of pseudaconitine not having at that time been arrived at, the method of purifying the base by conversion into crystallised nitrate not having then been found out.

The following numbers were obtained:—

A. Apopseudaconine obtained by the action of water at 140° for 24 hours—

0·2410 gram gave 0·5630 CO_2, and 0·1815 H_2O.

B. Another specimen similarly obtained—

0·2410 gram gave 0·5600 CO_2, and 0·1815 H_2O.

C. Prepared by alcoholic soda at 140° for 24 hours—

0·2460 gram gave 0·5690 CO_2, and 0·1860 H_2O.

	Calculated.		Found.		
			A.	B.	C.
C_{27}	324	64·16	63·71	63·36	63·10
H_{39}	39	7·72	8·37	8·37	8·40
N	14	2·77	—	—	—
O_8	128	25·35	—	—	—
$C_{27}H_{39}NO_8$	505	100·00			

§ 4. *Action of Acids on Pseudaconitine.*

When pseudaconitine is heated in contact with dilute or concentrated mineral acids, it quickly becomes saponified and altered, dimethylprotocatechuic acid being extractable by ether from the product of the action in larger or smaller quantity, according to circumstances; the saponification, however, does not seem to be as rapid as a rule as with alkalies; thus, solutions of pseudaconitine in excess of dilute hydrochloric, nitric, or sulphuric acid may be allowed to stand for weeks in the cold, and even gently warmed for some time without the formation of more than traces of (and often of not any) dimethylprotocatechuic acid; whilst if a pseudaconitine salt be diluted with water, and an alkali added in excess, on standing for some time (a few hours to a few days) dimethylprotocatechuic acid is always formed to a considerable extent, even in the cold. On heating to 100° a solution of pseudaconitine in excess of a mineral acid, saponification is brought about rapidly, especially with a concentrated acid; thus about 40 per cent. of the alkali is saponified on heating to 100° for 3 hours, with about 10 parts of concentrated hydriodic acid. No methyliodide is thus formed, and no protocatechuic acid is obtained, showing that

the dimethylprotocatechuic acid generated is not demethylised at 100° by hydriodic acid. Hydrochloric, hydrobromic, and sulphuric acids produce analogous results; the product of the continued boiling for some hours with dilute sulphuric acid does not reduce Fehling's solution. Organic acids, however, such as tartaric and acetic, act very differently; scarcely a perceptible trace of dimethylprotocatechuic acid is formed when pseudaconitine is heated to 100°, with a large excess of glacial acetic acid, or of almost saturated solution of tartaric acid for several hours; or even if boiled with moderately concentrated tartaric acid solution for several hours. Other changes, however, are produced by these organic acids; thus after 8 hours' heating to 100°, with nearly saturated solution of tartaric acid, the pseudaconitine becomes converted into *apopseudaconitine* by the reaction—

$$C_{36}H_{49}NO_{12} = H_2O + C_{36}H_{47}NO_{11}.$$

The product of the action was diluted with water and treated with caustic soda and ether: from the ethereal solution there separated on spontaneous evaporation crystals of apopseudaconitine so closely resembling the original base that it is somewhat difficult to distinguish them; apopseudaconitine, however, appears to be decidedly less extremely soluble in alcohol and ether, although its solubility in these menstrua is still considerable. When anhydrous it slightly frits at 100° (like pseudaconitine) and melts to a thick viscid mass at 102—103°, or slightly lower than pseudaconitine which fuses similarly at about 105°; when the two are compared side by side, it is distinctly seen that apopseudaconitine melts some 2° below pseudaconitine.

When crystallised from ether by spontaneous evaporation apopseudaconitine is represented by the formula $C_{36}H_{47}NO_{11},H_2O$; *i.e.*, it is isomeric with pseudaconitine deprived of its water of crystallisation: like the crystallised parent base it readily becomes anhydrous at 100°.

0·5645 gram of air-dry base lost at 100° 0·0160 = 2·83 per cent.
Calculated for $C_{36}H_{47}NO_{11},H_2O$ = 2·62 ,,
0·2310 gram of base dried at 100° gave 0·5480 CO_2 and 0·1685 H_2O.

The base furnishes a well-crystallised nitrate on rubbing with excess of dilute nitric acid, or on dissolving in sufficient dilute acid, adding a few drops of concentrated acid, and stirring vigorously. From the crystals of nitrate thus prepared the base was regenerated by means of soda and ether; of the resulting substance, 0·2745 gram dried at 100° gave 0·6445 CO_2 and 0·1925 H_2O.

	Calculated.		Found.	
C_{36}	432	64·57	64·69	64·03
H_{47}	47	7·03	8·10	7·79
N.....	14	2·09	—	—
O_{11}	176	26·31	—	—
$C_{36}H_{47}NO_{11}$ ..	669	100·00		

The gold-salt, when precipitated from weak solutions of the hydrochloride, is crystalline; when dried over sulphuric acid it can readily be crystallised from hot alcohol in minute anhydrous needles.

0·3005 gram gave 0·0585 Au = 19·46 per cent.
Calculated for $C_{36}H_{47}NO_{11},HCl,AuCl_3$ = 19·44 ,,

In order to see if inorganic acids also cause the dehydration of pseudaconitine as well as its saponification, pure pseudaconitine was heated with about 15 parts of an aqueous solution containing 5 per cent. of HCl to 100° for 8 hours. On shaking the acid liquid with ether, dimethyl protocatechuic acid was dissolved out to an extent indicating that about a twentieth part of the pseudaconitine used had been saponified. On adding soda and ether, and allowing to evaporate spontaneously, crystals formed, less readily soluble in alcohol and ether than pseudaconitine, giving rise to a crystalline gold-salt and a well-crystallised nitrate: these crystals, however, were slightly mixed with a non-crystalline base (presumably pseudaconine formed by the saponification); they were converted into nitrate, filter-pumped and washed with weak nitric acid; from the salt thus obtained the base was regenerated corresponding in all respects with the apopseudaconitine prepared by means of tartaric acid.

0·2475 gram dried at 100° gave 0·5815 CO_2 and 0·1825 H_2O.

	Calculated.	Found.
Carbon	64·57	64·08
Hydrogen	7·03	8·19

From these results there can be little doubt that the specimen of pseudaconitine prepared by Mr. Groves by means of alcoholic hydrochloric acid (§ I.) actually contained apopseudaconitine, formed by the action of the hydrochloric acid during the extraction.

Glacial acetic acid acts in a somewhat different fashion from aqueous tartaric acid: the elements of water are indeed removed from pseudaconitine, but the resulting apopseudaconitine is further acted on forming *acetyl apopseudaconitine* in accordance with the reaction

$$C_{36}H_{47}NO_{11} + C_2H_4O_2 = H_2O + C_{36}H_{45}(C_2H_3O)NO_{11},$$

just as morphine and codeine give rise to acetylated derivatives by similar treatment (Alder-Wright, this *Journal*, 1874, 1031). Pseudaconitine was heated to 100° for 8 hours with about 12 parts of glacial acetic acid: on diluting the resulting fluid with water, adding soda and agitating with ether, and allowing the ethereal solution to evaporate spontaneously, a well-crystallised base was obtained sensibly less soluble in alcohol and especially in ether than pseudaconitine, though still readily soluble in either menstruum. When air-dry it contains one proportion of water of crystallisation (like pseudaconitine and apopseudaconitine).

0·4955 gram of air-dry crystals lost at 100° 0·0130 gram ..... = 2·62 per cent.

Calculated for $C_{36}H_{46}(C_2H_3O)NO_{11},H_2O$.. = 2·47 ,,

0·2575 grm. of base dried at 100° gave 0·6080 CO_2 and 0·1850 H_2O.

	Calculated.		Found.
C_{38}.....	456	64·13	64·38
H_{49}	49	6·90	7·98
N	14	1·97	—
O_{12}	192	27·00	—
$C_{36}H_{46}(C_2H_3O)NO_{11}$	711	100·00	

In order to determine the degree of acetylation, 0·5970 gram of anhydrous base were dissolved in alcohol, exactly neutralised, and saponified in a soda-water bottle (at 100° for about 14 hours) with a measured excess of standard caustic soda solution. From the amount of soda neutralised the quantity of mixed acetic and dimethylprotocatechuic acids formed was calculated, being 0·2057 gram of a mixture of equivalent quantities of $C_9H_{10}O_4$ and $C_2H_4O_2$. The whole was then acidified and the acetic acid distilled off with water as long as any acid came over: by titration the distillate was found to contain 0·0510 gram of $C_2H_4O_2$. Finally the dimethyl protocatechuic acid (and a trace of resinous decomposition-product) was extracted from the residue in the distillation-flask by means of ether, and the ethereal solution evaporated to dryness and weighed after drying at 100°: the residue weighed 0·1590 gram, and when titrated by standard soda neutralised alkali equivalent to 0·1550 gram of $C_9H_{10}O_4$.

	Calculated.	Found. By titration.	By weighing.
Acetic acid.....	8·44	8·55	— —
Dimethyl-protocatechuic acid ..	25·59	25·96	— 26·63
Total acid	34·03	34·51	34·46

Acetyl apopseudaconitine forms a well-crystallised nitrate on stirring with excess of dilute nitric acid: the gold-salt is thrown down

in microscopic crystals from a dilute solution of the hydrochloride on adding auric chloride; it is readily crystallisable from hot alcohol, and is but sparingly soluble in cold alcohol. The anhydrous base melts at a somewhat higher temperature than pseudaconitine in a capillary tube, becoming a highly viscid transparent mass at about 115°, the melting point, like that of pseudaconitine, not being very distinctly marked: it slightly frits at 100°, however, on heating for some time.

§ 5. *Action of Organic Anhydrides on Pseudaconitine and Pseudaconine.*

It has been shown by one of us (this *Journal*, 1874, 1031), that whilst morphine furnishes, when treated with glacial acetic acid, an acetyl derivative containing only *one* acetyl group per 1 nitrogen symbol in the formula, it gives rise, by the action of acetic anhydride in excess, to a derivative containing twice as many acetyl-groups. In order to see if pseudaconitine behaves in a similar way, the anhydrous base was heated to 100° for an hour with twice its weight of acetic anhydride: to the colourless product a dilute solution of tartaric acid was added and the whole agitated with ether to remove any trace of resinoid bye-product. Soda was then added to the aqueous liquid and the whole agitated with ether. By spontaneous evaporation, crystals were obtained which on examination proved to be *identical with the acetyl apopseudaconitine* formed by the action of glacial acetic acid (§ 4), and not a more highly acetylated product: it melted at 115°; after drying at 100° 0·2615 gram gave 0·6180 CO_2 and 0·1875 H_2O.

	Calculated.		Found.
C_{38}	456	64·13	64·45
H_{49}	49	6·90	7·96
N.....	14	1·97	—
O_{12}	192	27·00	—
$C_{36}H_{46}(C_2H_3O)NO_{11}$	711	100·00	

On saponification, 0·7800 gram neutralised soda equivalent to 0·2710 gram of $C_9H_{10}O_4$ + $C_2H_4O_2$. On distilling off the acetic acid formed and titration, 0·0740 gram $C_2H_4O_2$ were obtained: from the residue by means of ether there was extracted 0·1970 gram of crude dimethyl protocatechuic acid, which on titration neutralised soda equivalent to 0·1965 gram $C_9H_{10}O_4$.

		Found.	
	Calculated.	By titration.	By weighing.
Acetic acid.....	8·44	9·48	— —
Dimethyl protocatechuic acid ..	25·59	25·19	— 25·26
Total acid	34·03	34·67	34·74

Hence the action of acetic anhydride on pseudaconitine is represented by the equation—

$$C_{36}H_{49}NO_{12} + 2(C_2H_3O)_2O = 3C_2H_4O_2 + C_{36}H_{46}(C_2H_3O)NO_{11}.$$

Benzoic anhydride yields precisely similar results, *benzoyl-apopseudaconitine*, $C_{36}H_{46}(C_7H_5O)NO_{11}$, being formed when benzoic anhydride is made to act on pseudaconitine, the reaction being—

$$C_{36}H_{49}NO_{12} + 2(C_7H_5O)_2O = 3C_7H_6O_2 + C_{36}H_{46}(C_7H_5O)NO_{11}.$$

Anhydrous pseudaconitine was mixed with twice its weight of benzoic anhydride and heated for two or three minutes to about 120° to render the whole fluid, the liquid being then kept at 100° for from one to two hours. On cooling and standing, the whole solidified to a crystalline mass (containing much benzoic acid): this was dissolved in a minimum of alcohol and largely diluted with ether, enough dilute solution of caustic potash added to set free any base present, and the whole well agitated and allowed to stand. The supernatant ethereal solution of new base, together with undecomposed benzoic anhydride and resinous bye-products (formed only in very small quantity), was then separated and agitated with dilute tartaric acid solution; and from the purified tartrate thus obtained, the base was regenerated by means of alkali and ether. On spontaneous evaporation, the ether left an indistinctly crystalline residue, which did not crystallise well on adding a few drops of alcohol and allowing to stand, but which was the hydrate of the benzoylated base, benzoyl-apopseudaconitine,

$$C_{36}H_{46}(C_7H_5O)NO_{11}, H_2O.$$

0·2730 gram of air-dry substance lost at 100°
0·0065 gram..... = 2·38 per cent.
Calculated for above formula ..... = 2·27 ,,
0·2665 gram of anhydrous base gave 0·6495 CO_2 and 0·1890 H_2O.

	Calculated.		Found.
C_{43}.....	516	66·75	66·46
H_{51}	51	6·60	7·87
N	14	1·81	—
O_{12}.....	192	24·84	—
$C_{36}H_{46}(C_7H_5O)NO_{11}$....	773	100·00	

On stirring up this base with just enough dilute nitric acid to dissolve it, adding a little concentrated acid, and rubbing well, a finely crystallised nitrate was formed: the gold-salt also crystallised from hot alcohol in well-defined anhydrous rosettes.

0·4700 gram gave 0·0840 Au ..... = 17·87 per cent.
Calculated for $C_{36}H_{46}(C_7H_5O)NO_{11},HCl,AuCl_3$ .. = 17·63 ,,

0·7190 gram of the base dried at 100° was saponified by alcoholic potash at 100° in a soda-water bottle; on evaporation, treatment of residue with hydrochloric acid and ether, and spontaneous evaporation, 0·2940 gram of mixed acids were obtained with a minute quantity of resinous bye-product; on titration, this neutralised alkali equivalent to 0·2890 gram of $C_9H_{10}O_4 + C_7H_6O_2$.

	Calculated.	Found. By titration.	Found. By weighing.
$C_9H_{10}O_4 + C_7H_6O_2$ ..	39·33	40·19	40·89

Analogous experiments with pseudaconine show that it is capable of yielding benzoylated and acetylated products; experiments on this subject are in progress, as also attempts to synthesise pseudaconitine from its saponification-products by inversion of the action taking place during saponification.

§ 6. *Constitution of Pseudaconitine and its Derivatives.*

From the circumstance that pseudaconitine splits up by a reaction of saponification into pseudaconine, $C_{27}H_{41}NO_8$, and dimethylprotocatechuic acid, known to be indicated by $C_6H_3\begin{cases}CO.OH\\O.CH_3\\O.CH_3\end{cases}$, it results that pseudaconitine may be written—

$$(C_{27}H_{40}NO_6)—O—CO.C_6H_3(OCH_3)_2.$$

The ready formation of apopseudaconitine by dehydration, and of acetyl and benzoyl apopseudaconitine by the action of glacial acetic acid and acetic and benzoic anhydrides, indicates moreover that pseudaconitine is a trihydroxylated base; so that the following formulæ may be ascribed:—

Pseudaconitine ..... $(C_{27}H_{37}NO_5)\begin{cases}OH\\OH\\OH\\O.CO.C_6H_3(O.CH_3)_2\end{cases}$

Apopseudaconitine ..... $(C_{27}H_{37}NO_5)\begin{cases}O\\OH\\O.CO.C_6H_3(O.CH_3)_2\end{cases}$

Acetyl apopseudaconitine.... $(C_{27}H_{37}NO_5)\begin{cases}O\\O.C_2H_3O\\O.CO.C_6H_3(O.CH_3)_2\end{cases}$

Benzoyl apopseudaconitine.. $(C_{27}H_{37}NO_5)\begin{cases}=O\\ -O.C_7H_5O\\ -O.CO.C_6H_3(O.CH_3)_2\end{cases}$

Pseudaconine..... $(C_{27}H_{37}NO_5)\begin{cases}-OH\\ -OH\\ -OH\\ -OH\end{cases}$

Apopseudaconine ..... $(C_{27}H_{37}NO_5)\begin{cases}=O\\ -OH\\ -OH\end{cases}$

The relationship between pseudaconitine and pseudaconine would therefore be expressible by applying to the former the unwieldy term "dimethylprotocatechuyl-pseudaconine": whence acetyl-apopseudaconitine would become "acetyl-dimethylprotocatechuyl-apopseudaconine," and so on!

Experiments now in progress indicate that aconitine from *A. napellus* has an analogous constitution; applying the term *aconine* to the base, $C_{26}H_{39}NO_{11}$, into which, together with benzoic acid, aconitine splits by saponification, the relationship of aconitine to this base is indicated by applying to the former the term "benzoyl-aconine," and the formula, $(C_{26}H_{38}NO_{10})—O—C_7H_5O$; which apparently may be further dissected, thus, $(C_{26}H_{35}NO_7)\begin{cases}-OH\\ -OH\\ -OH\\ -O.C_7H_5O\end{cases}$, aconitine being a trihydroxylated base.

Evidently the quadrivalent radicles, $C_{27}H_{37}NO_5$, and $C_{26}H_{35}NO_7$, of pseudaconitine and aconitine respectively are closely allied: experiments with a view to elucidating the "structure" of these radicles are in progress, though as yet no results of importance have been arrived at.

It is specially noteworthy that pseudaconitine is thus closely connected with the opium alkaloïds narceine, narcotine, and oxynarcotine, all of which split up, giving rise to substances which are derivatives of dimethyl-protocatechuic acid (Beckett and Alder-Wright, this *Journal*, 1875, 573; 1876, i, 281 and 461). Moreover it is remarkable that all the natural alkaloïds which have hitherto been split up by saponification-reactions yield acids of the aromatic series: thus with narcotine, narceine, oxynarcotine, pseudaconitine, aconitine, atropine (Kraut, *Jahresbericht*, 1865, 448), cocaine (Lossen, *ibid.*, 451), and piperine (von Babo and Keller). Experiments now in progress with the alkaloïds of Sabadilla seeds, however, show that the so-called "veratria" of commerce is a mixture of alkaloïds, two of which belong to the saponifiable class, one giving rise to the same dimethyl-protocatechuic acid as pseudaconitine, the other forming an acid of a

different kind, apparently identical, or isomeric, with *angelic acid*, $C_5H_8O_2$.

§ 7. *Other Bases contained in Commercial "Aconitine" from A. ferox.*

In the preparation of pure pseudaconitine nitrate as above described (§ 1) from the crude drug supplied by Messrs. Hopkin and Williams, there was obtained a nitric acid mother-liquor from which no crystals could be obtained, but which contained a considerable amount of alkaloïdal matter. On dilution with water, this deposited some resinoid matter; from the filtrate from this alkalies threw down a copious white amorphous precipitate. The precipitate thus obtained with sodium carbonate dissolved readily in ether, but furnished no crystalline base or salt by any kind of treatment tried. The base recovered from the ethereal solution as a varnish, and dried at 100°, contained—

Carbon	63·37
Hydrogen	8·01
Nitrogen	3·21

and on saponification it formed dimethylprotocatechuic acid to the extent of 19·7 per cent. (calculated from weight of acid obtained from ether; 18·5 per cent. by titration), from which it would appear it consisted largely of some substance closely allied to pseudaconitine, not improbably an alteration-product formed during extraction, and possibly identical with the amorphous base obtained by heating pseudaconitine acetate (§ 1). The sodium carbonate filtrate from this precipitate was evaporated to dryness, and the residue treated with alcohol; a quantity of brown amorphous alkaloïdal matter was thus dissolved out: on evaporating to dryness and treating with water, a considerable portion dissolved, consisting apparently of impure pseudaconine, as it formed only minute amounts of dimethyl protocatechuic acid on saponification.

From these results it is evident that the commercial alkaloïd is liable to be admixed with considerable quantities of amorphous bases: it was estimated that about a fifth of the material obtained from Messrs. Hopkin and Williams consisted of such substances; although the amorphous bases were not destitute of physiological potency, yet they appeared to produce far less lip-tingling, &c., than pure pseudaconitine. The nitrate of pseudaconitine being almost insoluble in nitric acid containing 8 to 10 per cent. of HNO_3, it would appear desirable that only the crystallised salt, or the alkaloïd thence regenerated, should be prepared for medicinal use, which could readily be accomplished in practice.

XX.—*On a Simplification of Regnault's Method for Determining Boiling Points with small quantities of Substance.*

By H. Chapman Jones, F.C.S.

The want of a method of determining boiling points by which a perfectly definite result can be obtained by the expenditure of only a moderate amount of time and trouble, and the employment of only a small quantity of the substance under investigation, has probably been felt by many. The disadvantages of the ordinary process are several, the chief being the varying conditions under which different experimenters work, and the necessity of vaporising a considerable quantity of the substance.

The boiling point of a body may be defined as the temperature at which the tension of its saturated vapour is equal to the standard atmospheric pressure. The first method that suggests itself for determining this temperature would be to introduce a small quantity of the substance into a barometer tube, filled with mercury, and inverted in a reservoir of the same metal, and then to heat the experimental tube, noting the temperature at which the mercury is at the same level outside and inside the tube. But such an experiment may be greatly simplified. If a syphon barometer tube is used, the separate cistern is dispensed with, and as it is only needed to observe the temperature at which the mercury stands at the same level in both limbs, the tube may be very greatly reduced in length. Practically, a piece of ordinary quill tubing, about 4 mm. internal diameter, and 200 mm. (8 inches) long, bent upon itself, so that the open end extends at least 15 mm. beyond the other, which is closed, is all that is necessary (*vide* Fig. 2). For the sake of convenience such a tube will in future be called a *tension-tube*.

The filling of these tubes with mercury, and the introduction into the closed end of a drop of the liquid to be examined, was the first difficulty of importance. I found that it was possible, by the exercise of a considerable amount of patience and perseverance, to charge a tension-tube, and keep it pretty free from air, by filling it with mercury, except a small space at the open end, then adding the substance. closing the tube, and inverting, &c., exactly after the manner of working with a bent eudiometer. Such an operation, however, is far too uncertain and tedious to be practically useful. I therefore tried to introduce the substance at the end of the tension-tube at which it was to remain, by means of a capillary opening. As this method has some advantages which will occasionally, perhaps, render it preferable to the one subsequently described, I will give the details of the manipulation.

The tube is made as before directed, but instead of closing one end, it is drawn out to a capillary tube, about 60 mm. long, and bent as shown, Fig. 1. Mercury is then poured into the tube, until it is nearly full, when it is examined to see if any air bubbles remain in the

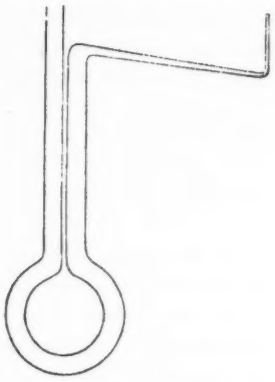


FIG. 1. ½ size.

limb that is to be closed. Such bubbles can easily be removed by tapping or gently warming the tube, or, if they adhere obstinately, by emptying and refilling. When the tube is free from bubbles, mercury is added, till it begins to drop from the capillary tube, and stands up above the walls of the tube at the other end. The damp thumb is now pressed upon the wide end, and should drive out more mercury from both ends of the tube. The apparatus is next inverted, and the capillary opening introduced below the surface of the liquid for examination; then the thumb should be relaxed a little, and mercury allowed to flow out till the substance is drawn into the capillary tube, and occupies 30 or 40 mm. of it. A little air is then drawn in, and the capillary tube sealed in a small flame. The mercury is now removed from the open end down to the bend, by means of a pipette, and the bubble of air in the capillary tube reduced in size, by gently warming to expand it, and then re-sealing as close as possible to the liquid. This operation may be repeated, but by no means have I been able to get quite rid of the air. This bubble, which should not be larger than a pin's head, entirely prevents any disposition of the substance to become overheated in the bath employed, because of its adhesion to the glass, but at the same time it lowers the apparent boiling point.

This method has one other great disadvantage, namely, that it cannot be used with safety when dealing with substances that are changed on ignition. The approximate amount of error to be expected from these causes will be seen from the three following cases, where

the upper figures show the true boiling point (determined by the method subsequently described), and the middle row of figures the results obtained by the method just detailed. In the 1st. CS_2, the bubble was not reduced at all; in the 2nd. it was reduced as far as possible by the method given above. The greater difference in the case of ethylic iodide may be attributed to the change brought about in a small quantity of its vapour by the operation of sealing off the capillary tube.

	CS_2.	CS_2.	C_2H_5I.	OH_2.
	46·2	46·2	72·2	100·0
	45·9	46·0	70·7	99·3
Difference	·3	·2	1·5	·7

The only way in which I have succeeded in charging tension-tubes without chance of failure, and with perfect elimination of air, is by driving out the air by the vapour of the substance itself. This is effected by introducing about two drops of the liquid to be examined into the tube, running it round to the closed end, then introducing the open end into some mercury contained in a small porcelain crucible. This arrangement, supported by a suitable sling, made of copper wire, is lowered into a water or paraffin bath, according to circumstances (see Fig. 2), and the temperature gradually raised. The air of the tension-tube is thus driven out in bubbles, which rise through the mercury and the liquid in the bath; the air is, of course, followed by

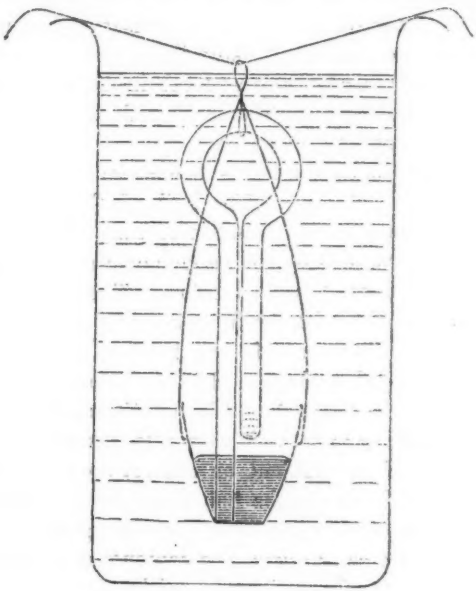


FIG. 2. ½ size.

the vapour of the substance. These bubbles come off with increased rapidity as the temperature of the bath nears the boiling point of the body used, and at about from 4° to 6° above it, there is a very marked increase, the action becoming violent if pushed much further. By observing the temperatures at which these changes take place, the boiling point of the substance may be ascertained to within 2° or 3°, a precaution which should never be omitted, as it saves subsequent trouble. When enough vapour has escaped to sweep out all the air, the bath is allowed to cool, or, if the temperature is not above 50° or 60°, the tube with the crucible containing mercury may be at once removed from the bath. In either case as the vapour in the tube condenses, the mercury rises, and completely fills it, except the space occupied by the drop of liquid at the top of the bend. The tension-tube is now released from the sling, and then removed from the crucible of mercury, and turned over by one operation, taking care that the closed limb shall be uppermost, so that the liquid may rise into the closed, and not into the open end. If the water (or paraffin) and mercury are now removed from the open limb by means of filter paper (or cold wire) and a pipette, the tube is ready for use. This method of filling a tension-tube, or rather of making it fill itself, is exceedingly simple in manipulation, and perfectly satisfactory. A tube so filled, after nine days had elapsed, during which it had been used two or three times, did not show the slightest evidence of any air having gained access to the closed limb, and could be heated a degree or two above the boiling point of the liquid without vaporisation taking place.

We now pass to the method of using these tubes. The temperature at which the mercury is at the same level in both limbs, will be the boiling point of the substance. To ascertain that temperature, the tube must be introduced into a bath of transparent liquid contained in a glass vessel, so that the closed end is below the surface, and the open end is freely exposed to the air. The bulb of the chief thermometer should be brought as close as possible to that portion of the closed limb which will be occupied by the vapour of the body, and a second thermometer arranged as described below. The temperature is then gradually raised, and the tube carefully watched as it approaches the boiling point of the substance. If the level of the mercury does not sink as soon as you judge that it should, the open end of the tube, which projects from the bath, should be gently tapped vertically by a hard substance (glass or metal). This gentle jerk will entirely obviate the difficulty. But if by accident or neglect the temperature of the bath has risen 2° or 3° above the boiling point of the substance, and consequently the mercury sinks with increasing instead of with diminishing rapidity, we can prevent the contents of the tube from being driven out, and the experiment lost, by raising the closed end a little

out of the bath, and lowering it into the bath again only as the temperature falls. (It will be observed that if the tube is filled by the second method and is free from air, the approximate boiling point is ascertained during the filling.) With common care, however, such an accident will never occur, but the mercury in the closed limb will gradually sink, until it is lower than the mercury in the open limb; on cooling, the mercury will rise again, and so by alternately heating the bath and allowing it to cool, the two mercury levels can be made to pass one another any number of times. Each time that the levels correspond, the temperature is noted. Six is a very convenient number of such observations to make, three as the bath is rising in temperature, and three as it is cooling. It is perfectly easy to keep these oscillations within half a degree on each side of the boiling point, and $1\frac{1}{2}^{\circ}$ on each side of it should be the maximum. The average of six such observations may be taken as the uncorrected boiling point, unless the first temperature evidently disagrees with the rest, when the first two observations are neglected, and two others substituted for them. This error will occur when the temperature of the bath has been raised too quickly, so that the tension-tube, with its contained mercury, has not been able to keep pace with it.

The tube, when done with, may be labelled and preserved, if worth while, so that the observations can be confirmed at any future time.

The boiling point so determined can be regarded only as approximate until it is corrected, and as all the boiling points given in this paper have been reduced to standard conditions, to make them comparable, it may be well to state here the exact corrections that have been applied. It is necessary to observe the height of the barometer, and the temperature of the air, and thus to get the height of the barometer at 0° C.; also to observe the mean temperature of that portion of the thread of mercury in the thermometer that is not immersed in the bath. To ascertain this temperature a second thermometer is used, the bulb of which is placed half way between the level of the liquid in the bath and the top of the mercury in the chief thermometer. Every time the temperature is to be taken, both thermometers must be read; then the number of degrees of the mercury of the chief thermometer that are not in the bath is to be multiplied by the difference in temperature between the two instruments, and the product multiplied by ·0001545 (the average coefficient of the apparent expansion of mercury in glass); the result is to be added to the temperature indicated by the chief thermometer, to obtain the real temperature. If the work is carried out as above described, there will be six such actual temperatures obtained, the average of which gives the boiling point under the pressure observed.

The correction for pressure is made by multiplying the number of

University of Michigan

mm. by which it differs from 760, by ·037 (that is, the fraction of a degree by which the boiling point of water varies for each mm. of barometric pressure, starting at 760 mm.), and adding the result to or subtracting it from the temperature observed, according to whether the pressure is below or above the normal pressure. A temperature so obtained is designated simply the *boiling point*.

I have made a good many experiments to ascertain the degree of accuracy that may be expected by the use of this method, and to show the effects of varying circumstances upon it. In these experiments I have carefully avoided any refinement of apparatus, or the spending of an undue amount of time over each operation, so that the results truly show the applicability of the process to the ordinary requirements of a laboratory, where the observation of boiling points is but of rare occurrence.

The apparatus used was the following:—

A thermometer by Negretti and Zambra, graduated from −5° to 105° C., each degree being divided into 5 parts. This was compared with a Kew standard at the ordinary temperature and found correct, and it registered 99·8—99·8—99·9, instead of 100, for the boiling point of water. ·2° is therefore added to its indications at about 100, and a corresponding correction is made for other temperatures. Its readings are given to ·1°, but the last figure must not be taken as absolute; the error may, however, be considered as less than ·1°.

An ordinary thermometer divided into single degrees graduated up to 360°, which was found fairly correct.

A beaker of a little more than half a litre capacity, as a water-bath, and one about half its capacity for the paraffin-bath. It would have been better if the size of the paraffin-bath had been increased. These were placed on a thick iron plate, or a piece of tinned iron (tinplate) supported on a tripod, and warmed by means of a Bunsen burner.

The two slings used for supporting the apparatus were made out of copper wire, the fingers being the only tools.

Bisulphide of carbon was the first substance employed. It is stated to boil at "46·6° under *ordinary* pressure." A small quantity of it was digested with sodium and then distilled without visible ebullition, by placing the retort containing it in warm water. The great variations of the barometer in November last, enabled me to make observations at very different pressures. The following are the temperatures observed *for the different pressures*, the lowest line being the boiling point deduced from each experiment:—

Pressure in mm.....	736·0	744·5	752·0	762·0
B.P. at above pressure.	45·1	45·5	46·0	46·3
B.P. at 760 mm.	46·0	46·1	46·3	46·2

Each of these temperatures is the average of from 5 to 10 observations, made as before described, the greatest difference between any two observations in any one series being ·2°. The observations in any one series are often all exactly alike, and could almost invariably be made so by working a little more slowly. The following is a specimen of what may be expected, the second decimal place being caused by the correction for exposed thread of mercury in the thermometer. The 1st, 3rd, 5th, &c., were taken as the temperature of the bath was rising; the 2nd, 4th, 6th, &c., as it was falling:—

46·04—45·90—46·04—46·00—45·99—45·95—45·99—45·99—
45·99—45·99.

A sample of ethylic iodide, which I believe is pure, was tested by this method, and its boiling point found to be 72·2°. A determination by Dr. Frankland (when corrected for pressure) gave 72·1°, when the thermometer bulb was in the vapour, and 72·7 when immersed in the liquid.

The entire time occupied by the above determination (including the making of the tension-tube) was $1\frac{3}{4}$ hour, much of which time was occupied in heating the water-bath, no attention being then necessary.

Water was the next substance experimented with. Two determinations of its boiling point made by fixing the thermometer with its bulb a little above the surface of some water kept rapidly boiling in a flask, gave 100·1° and 100·0°. These experiments were made quite independently at an interval of ten days. The boiling point of water, taken by means of a tension-tube and a paraffin-bath, was found to be 100·0°.

Some phenol was prepared from solid carbolic acid by distilling and collecting when the distillate was homogeneous. The portion collected came over between 183° and 185°. The phenol was liquefied by immersing the bottle containing it in warm water; the tension-tube was slightly warmed, and a drop or two introduced by means of a small pipette. The boiling point was found to be $183\frac{1}{2}$°, but at this high temperature the tension of mercury-vapour becomes appreciable (= 11 mm.); so, deducting this from the barometric pressure, and recalculating, we get 184° as the boiling point.

This agrees with a determination by Scrugham, who found the boiling point to be 184°, whereas Laurent made it 187° to 188°.

The next substance employed was benzoic acid. This body is stated to melt at 121·4° and boil at 250°. The tension-tube was charged as usual, the acid vaporising abundantly at 256°. The substance solidified on cooling at the bend of the tube, but was driven to the top of the closed limb without the least difficulty by gently warming it in a small flame. As the paraffin became practically opaque by

heating it to this high temperature, the experiment could not be finished; but if a suitable substance were found to replace it, the only difficulty of these experiments at such temperatures would be surmounted. Paraffin is suitable for use up to about 200°.

Inasmuch as substances operated on are not always pure, it is well to know the effect that solids in solution, liquid impurities, &c., have upon the boiling point of a body. The following experiments were undertaken with this end in view.

A strong but not saturated solution of calcic chloride gave a boiling point of 119½°.

A saturated solution of common salt was then experimented with as follows. An ounce or two was introduced into a capacious flask, some scraps of platinum dropped in, and the solution heated till it boiled briskly. A thermometer with its bulb immersed in the liquid was stationary at 108¼°, and when raised so that the bulb was about 1½ inch from the surface of the liquid, it fell only ¼ or ½ a degree. The boiling point taken by means of a tension-tube was found to be 107¼°. A minute bubble of air was afterwards discovered in the tube, which accounts for the discrepancy observed. The separation of solid salt tended to prevent a very satisfactory operation.

These experiments show that solid substances in solution tend to raise the boiling point of the liquid, that is, the tension of the vapour of the solvent is lowered.

A mixture of alcohol and water gave a boiling point of 82·0°, showing that a mixture of liquids that mix with one another, or that are mutually soluble in each other, gives a boiling point intermediate between the boiling points of its constituents.

Some carbonic disulphide and water were introduced into a tension-tube, and the apparent boiling point determined. It was found to be 43·4°, showing that a mixture of liquids which are not soluble in each other, gives an apparent boiling point lower than that of either separately, that is, the tensions of their vapours are *added*.

By deducting from the pressure observed, the equivalent for the tension of water vapour at the observed temperature, and recalculating for the reduced pressure, we obtain from this experiment 45·7° for the boiling point of CS_2, its actual boiling point being 46·2°.

It was not considered necessary to multiply these experiments, as they agree perfectly with well known laws.

In conclusion, I think that the advantages of this method will be found to be:—

1st. The obtaining of definite, constant, and perfectly comparable results.

2nd. Diminution of error of observation, as several readings can be taken.

3rd. The fact that a single drop of any substance is all that is needed.

4th. That the method can at any time be rendered more exact, by little refinements that will be obvious to any experimenter.

Postscript.—On communicating the results of the work detailed above to Dr. Frankland, he was good enough to tell me that spermaceti could be used at higher temperatures than paraffin. I find that spermaceti will bear heating up to nearly 300° C. without losing its transparency or evolving an inconvenient amount of vapour; the only drawback to its use for all temperatures over 80° or 90° is that it would probably be more readily acted upon by the vapour of substances passing through it than paraffin.

Dr. Frankland was also so kind as to give me small quantities of the following substances to examine by my method.

No. 1 was a sample of methylic iodide, and No. 2 a sample of ethylic diethoxalate, $\left(\begin{smallmatrix}(CC_2H_5)_2.OH\\CO.O(C_2H_5)\end{smallmatrix}\right)$, B.P. stated as 175° C. (barometric pressure not known). Both these were the ordinary preparations of the laboratory. No 3 was a sample of commercial benzol, known to be impure. The boiling points I found were as follows:—

1.	2.	3.
42·8	175¾	86·9

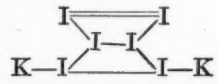
These results fully confirm the usefulness and trustworthiness of the method.

XXI.—*On certain Polyiodides.*

By George Stillingfleet Johnson, Daniell Scholar of King's College, London.

In December, 1876, I read to the Chemical Society a paper in which I described the compound now known as triiodide of potassium. The graphic formula for this body, on the assumption that iodine is triatomic, may be thus represented, if its formula be taken as KI_3:—

But, inasmuch as the compound HgI_6 is well known, it occurred to me that the triiodide of potassium might perhaps be more correctly represented as dipotassic hexiodide, with the formula K_2I_6. In this case its graphic formula would be written thus:—



Now, if K_2I_6 be the true formula for the salt, it is evident that substitution-compounds might be obtained by displacing one atom of potassium with one atom of some other monatomic element, or perhaps of two atoms of potassium in K_4I_{12} by one atom of a diatomic element. With the view then to prepare some such substitution-compounds, I made the investigation whose results are now recorded.

The metal *silver* was first selected, as being monatomic, and having an iodide freely soluble in strong solutions of potassic iodide.

My first attempt was to make a solution containing silver, potassium, and iodine in the proportions required by the formula $AgKI_6$. The iodides of silver and potassium were readily dissolved in the proportions indicated, and the boiling aqueous solution prevented from depositing crystals on cooling by the addition of a little alcohol; but, long before the required amount of free iodine had been dissolved, a large quantity of the silver was always precipitated as AgI, and this precipitate could only be dissolved by a further addition of potassic iodide. Moreover, the constituents of $AgKI_6$ could not be brought into solution together by first mixing them in the dry state, and then stirring with a small quantity of water.

Iodides of silver and potassium and free iodine were next dissolved in proportion to form AgK_3I_{12}. All the constituents were easily dissolved in a small quantity of water by the aid of heat, and nothing separated out on cooling. When this solution was allowed to evaporate slowly over sulphuric acid, crystals of argento-potassic iodide, slightly coloured by free iodine, first separated, next crystals of potassium triiodide, slightly contaminated with silver iodide, and, finally, crystals containing from 10 to 12 per cent. of argentic iodide and 53 per cent. of iodine, which was set free as vapour by the application of a gentle heat. The formula indicated by the analysis of these crystals is $AgK_3I_{12}.KI$, which requires 12·27 per cent. of argentic iodide, 34·69 per cent. of potassic iodide, and 53·04 per cent. of iodine in excess over that contained in KI and AgI. Accordingly, a solution was made containing the above ingredients in the proportions mentioned. No argento-potassic iodide or potassium triiodide separated from this solution on evaporation; but three sets of crystals were removed from it, all having the same composition. The results of analysis are as follows:—

Analysis of Crystals II:—

The *iodine*, in excess of that contained in KI and AgI, was determined by titration with a standard solution of hyposulphite (thiosulphate) of soda, starch being used as an indicator.

(*a.*) 0·292 gram required 11·7 c.c. of hyposulphite solution, of which 1 c.c. is equivalent to 0·0127 gram iodine.

This represents 0·14859 gram iodine, or 50·88 per cent.

(*b.*) 0·345 gram required 13·8 c.c. of the above hypo-solution, equivalent to 0·17526 gram iodine, or 50·8 per cent.

Analysis of Crystals III:—

(*a.*) 0·513 gram required 21·45 c.c. of hyposulphite solution, of which 1 c.c. = 0·01212 gram iodine.

This number is equivalent to 0·259974 gram iodine, or 50·67 per cent.

(*b.*) 0·467 gram required 19·55 c.c. of the above solution of hypo, equivalent to 0·236946 gram iodine, or 50·73 per cent.

The mean of these numbers gives 50·77 per cent. of iodine in excess over KI and AgI.

In order to determine the silver iodide, a weighed portion of the compound was treated with a slight excess of solution of sulphurous acid gas, the yellowish liquid thus formed diluted freely with water, and the argentic iodide allowed to settle, collected on a weighed filter, washed, and weighed. The results were as follows:—

(*a.*) 2·001 grams (Crystals II) yielded 0·234 gram AgI, or 11·694 per cent.

(*b.*) 2·783 grams (Crystals III) gave 0·324 gram AgI, or 11·642 per cent.

The mean of these numbers is 11·668 per cent.

The *potassium* in the compound was estimated as *sulphate*. A weighed portion of the crystals was treated with sulphurous acid in excess, and the whole of the iodine precipitated by nitrate of silver. The argentic iodide was next removed by filtration, and excess of silver separated from the filtrate by hydrochloric acid and a second filtration. The clear liquid thus obtained was evaporated to a small bulk, mixed with dilute sulphuric acid, and evaporated to dryness. The residue thus obtained was treated with carbonate of ammonia, and ignited till its weight was constant.

(*a.*) 3·718 grams (Crystals II) gave 0·642 gram K_2SO_4, equivalent to 0·288193 gram K, or 7·75 per cent.

(*b.*) 2·944 grams (Crystals III) gave 0·511 gram K_2SO_4 = 0·2293879 gram K, or 7·79 per cent.

The mean of these numbers gives 7·77 per cent. potassium. The *total iodine* contained in the salt was ascertained by addition of solution of sulphurous acid in excess, and precipitation by nitrate of silver, the argentic iodide being collected on a weighed filter, washed, and weighed. The results are as follow :—

(*a.*) 5·123 grams (Crystals II) gave 7·812 grams of argentic iodide, equivalent to 4·222 grams iodine, or 82·41 per cent.

(*b.*) 2·783 grams (Crystals III) gave 4·239 grams AgI = 2·291 grams I, or 82·32 per cent.

The mean of these numbers gives 82·36 per cent. of iodine. The *water* present was determined by deducting the amount of iodine in excess over KI and AgI, as determined by titration with hyposulphite, from the total loss which the crystals underwent when gently heated. The compound loses about half its water by efflorescence when dried over sulphuric acid, but may be dried without loss of water over chloride of calcium.

(*a.*) 2·307 grams lost 1·266 grams by heat = 54·87 per cent., which leaves 4·21 per cent. H_2O.

(*b.*) 2·555 grams lost 1·405 grams by heat = 54·99 per cent., leaving 4·33 per cent. H_2O.

The mean of the above numbers gives 4·27 per cent. H_2O. The formula of the potassio-argentic polyiodide determined from the above analyses is—

$$AgK_3I_{12}.KI + 5H_2O.$$

The concordance between the results of analysis and the requirements of the formula will be seen in the following table :—

$AgK_3I_{12}.KI.5H_2O.$

	Theory.	Found.	
Iodine (total).....	82·33	82·36	82·41 82·32
Potassium	7·8	7·77	7·75 7·79
Silver	5·38	5·36	Mean of AgI determinations
H_2O	4·48	4·27	42·1 4·33
	99·99	99·76	

	Theory.	Found.	
Iodine (free to act upon starch)	50·66	50·77	50·88 50·8 50·67 50·73
KI	33·13	33·007	Mean of two K determinations.
AgI	11·72	11·668	11·694 11·642
H_2O	4·48	4·27	4·21 4·33
	99·99	99·715	

Though this salt is efflorescent when placed over strong sulphuric acid, it nevertheless deliquesces in the air. A small quantity of water dissolves it entirely, and it may be recrystallised from this solution by evaporation over sulphuric acid. The crystals occur in groups with a stepped arrangement; are almost black, with a peculiar lustre, and are very deliquescent. When treated with excess of water, iodine and argentic iodide are separated, whilst potassic iodide and some free iodine remain in solution.

The formula of the above compound might be written thus: $AgKI_6.K_2I_6.KI.5H_2O$, if we assume that the formula of the periodide of potassium is K_2I_6; one atom of potassium in K_2I_6 being displaced by one atom of silver; or the formula might be written thus, $4KI_3.AgI.5H_2O$, on the assumption that the salt is a *molecular* compound.

Seeing the close analogy between the metals potassium and thallium as regards their behaviour with iodine, each forming two iodides, in which the iodine appears to be of different atomicity, viz.:—

TlI corresponding with KI
and Tl_2I_6 „ „ K_2I_6,

though, if the formulæ of the lower iodides be doubled, they, too, may be graphically represented, on the assumption that *I* is triatomic, thus:—

K—I=I—K.

My next endeavour was to produce a compound between the periodides of thallium and potassium, having some such formula as $K_2Tl_2I_{12}$: in this, however, I was not successful, the only compound of potassium, thallium, and iodine, which appears to have a definite nature, being one which was discovered by Willm (*Jahresb.*, 1864, 251). I reproduced this salt and analysed it, but the results of my analysis point to a somewhat simpler formula than that proposed by

Rammelsberg (*Pogg. Ann.*, cxlvi, 592), viz., $3KI.2TlI_3 + 3H_2O$, whilst they have led me to adopt the same formula as the discoverer, viz., $TlI_3.KI$, except that I believe the salt to contain two molecules of water of crystallisation, my formula standing thus:—

$$KI_3.TlI + 2H_2O.$$

The iodine in excess of that present as TlI and KI, and the water of crystallisation, were determined by the application of a gentle heat to a known weight of the crystals, and by weighing the residual iodides of potassium and thallium. The results are as follow:—

(*a.*) 1·692 grams of the dried crystals lost 0·625 gram, or 36·93 per cent.

(*b.*) 0·6475 gram lost 0·2385 gram, or 36·83 per cent.

(*c.*) 2·8515 grams lost 1·052 grams, or 36·89 per cent.

The mean of the above determinations is 36·883 per cent.

The *thallious iodide* was estimated by washing the yellow mass, left after igniting the crystals, with boiling water upon a weighed filter, drying at 100° C., and weighing the residual iodide of thallium.

(*a.*) 0·6475 gram of the dry crystals gave 0·271 gram TlI, or 41·85 per cent.

(*b.*) 1·872 gram gave 0·793 gram TlI, or 42·3 per cent.

Mean 42·105 per cent. Discrepancy due to sparing solubility of the thallious iodide.

The following analysis was made with a view to discover the relative proportions of potassium and thallium in the salt. The iodides of these two metals, left after igniting a known weight of the dried crystals, having been accurately weighed, were converted into sulphates by evaporating to dryness, after the addition of excess of dilute sulphuric acid; and the weight of the mixed sulphates was noted. 2·8515 grams of the dry salt gave 1·7995 grams of iodides of potassium and thallium after ignition. The weight of mixed sulphates obtained from these iodides was 1·228 grams. Now if the formula of the salt be, as I believe it is, $KI_3.TlI + 2H_2O$, or $K_2I_6.2TlI + 4H_2O$, the above quantity of it would yield 1·226 grams of sulphates of thallium and potassium.

The thallium was precipitated from the aqueous solution of these mixed sulphates as basic chromate (Tl_2CrO_4), by the addition of solution of bichromate of potash and a slight excess of ammonia, and the chromate of thallium was collected and weighed.

0·937 gram of Tl_2CrO_4 was thus obtained, which corresponds with 0·7288 gram of thallium, or 25·55 per cent. The formula requires 25·91 per cent.; but this discrepancy is accounted for by the sparing solubility of the basic chromate of thallium.

The formula, $K_2I_6.2TlI + 4H_2O$ requires—

	Theory.	Found.
$\dot{1} + H_2O$	36·84 per cent.	36·883 { 36·93 36·89 36·83
TlI	42·05 „	42·105 { 41·85 42·36

Of course there is no proof that the composition of the above salt is not $Tl_2I_6.2KI + 4H_2O$, for whether thallious iodide be dissolved in solution of potassium triiodide or thallic iodide (TlI_3) in solution of potassic iodide, the crystals which separate have the same form and composition, the only point worthy of notice being that the former solution is effected much more readily than the latter; but it seems clear that one of these two formulæ must be accepted in preference to those of Willm and Rammelsberg.

Before the isolation of potassium triiodide, Piffard (*Zeitschr. Chem. Pharm.*, 1861, 151) supposed that the solution of iodine in aqueous potassium iodide contained a definite periodide, because it gave a dark-coloured precipitate with a solution of acetate of lead, which precipitate, according to him, did not part with iodine to solvents.

On the other hand, Dosios a. Weith (*Zeitsch. f. Chem.*, 1869, 379) found that this dark precipitate did give up iodine to solvents, and hence regarded it as PbI_2, mixed with free iodine, but did not analyse it. (See *Watts' Dict.*, 2nd Sup., p. 677.)

I obtained the above precipitate, collected it, washed it, and pressed it between blotting-paper. When dry, it appeared as a dark purple powder, which certainly imparted a purple tinge to carbon disulphide; but it seemed to me more important that it was constantly decomposed by washing, for lead could always be found in the washings, and its composition was variable.

It occurred to me, however, to employ a different solvent, viz., alcohol in the preparation of this compound. Accordingly I made a saturated solution of sugar of lead in boiling alcohol, and added it whilst hot to a strong alcoholic solution of potassium triiodide; a very slight precipitate (PbI_2) separated at once; the hot liquid was rapidly filtered, and deposited on cooling a number of small but well-formed crystals.

The salt thus formed is permanent in the air, *i.e.*, it is not in the least deliquescent. It may be kept indefinitely in well-stoppered bottles without change, but it evolves the odour of iodine, and, if exposed, very gradually loses its lustre. The crystals appear to be square prisms, or elongated cubes, and are usually aggregated in clumps. By recrystallisation from hot alcohol, however, and gradual evaporation of the mother-liquor over sulphuric acid, I succeeded in obtaining some fairly large isolated crystals. Each crystal has six

faces, of which two (always opposite one another) have a dark purple reflection, whilst the remaining four reflect a greenish-golden light; they appear to be dichroic. The lustre is almost metallic; the crystals yield a dark-brown powder. When the crystals are dropped into water, they undergo no change in form, but the water is coloured faintly brown, just as it would be by free iodine; whilst the crystal loses its lustre and acquires a dull brownish appearance. The salt may be entirely, though slowly, dissolved in cold saturated solution of potassic iodide, ammonic chloride, or ammonic acetate. It also dissolves gradually in cold aqueous alcohol, but more readily in hot alcohol, from which it may be recrystallised easily.

The *specific gravity* of the compound could only be approximately ascertained, since no liquid could be found which was quite without action on the salt. By weighing in dilute sulphuric acid, which gave it a protecting coating, consisting chiefly of iodine and $PbSO_4$, the number 3·084 was obtained.

The formula of the salt is somewhat complicated, as will be seen from the following results. The elements present are Pb, C, H, O, K, and I.

The *lead* was determined as sulphate.

(*a.*) 1·5408 grams of the dry crystals, treated with excess of sulphuric acid, evaporated to dryness, gave a residue which (after being digested with boiling water for some hours, washed with boiling water, and dried on a weighed filter at 100° C.) weighed 0·750 gram. This is equivalent to 48·67 per cent. $PbSO_4$, or 33·249 per cent. Pb.

(*b.*) 0·7915 gram, dissolved in alcohol and water, diluted and precipitated with solution of sulphurous acid, the precipitate being washed and weighed as before, gave 0·384 gram of $PbSO_4$, or 48·51 per cent., equivalent to 33·14 per cent. Pb.

The *carbon* was estimated as CO_2 by combustion with chromate of lead, the *hydrogen* being collected and weighed as water at the same time; rolled copper wire was employed to collect the vapour of iodine, which was plentifully evolved during the combustion with chromate of lead.

(*a.*) 0·5585 gram of the powdered salt gave 0·057 gram H_2O, and 0·176 gram CO_2, equivalent to 0·0063 gram hydrogen and 0·048 gram carbon, or 1·112 per cent. hydrogen and 8·59 per cent. of carbon.

(*b.*) 1·673 grams gave 0·176 gram water, and 0·532 gave CO_2, equivalent to 0·01844 gram hydrogen and 0·14509 gram carbon, or 1·1 per cent. of hydrogen and 8·67 per cent. of carbon.

The *potassium* was determined as *sulphate*. The powdered salt was mixed with pure oxide of copper and ignited, first gently, then strongly, till fumes of iodine ceased to be evolved. The resulting mass was digested in boiling water for many hours; and the turbid liquid

thus obtained was filtered and evaporated to dryness after the addition of sulphuric acid, bisulphate being converted into neutral sulphate by igniting the residue with ammonic carbonate.

(*a.*) 3·3815 grams of the powdered salt yielded 0·35 gram. K_2SO_4 = 10·35 per cent., or 4·646 per cent. of potassium.

(*b.*) 2·307 grams of the recrystallised powdered salt gave 0·241 gram K_2SO_4, equivalent to 10·446 per cent. of sulphate of potash, or 4·69 per cent. of potassium.

The *total iodine* present was ascertained by mixing a known weight of the dry crystals with excess of a solution of pure ferric chloride, free from Cl and HNO_3 (prepared by passing chlorine over red-hot iron filings), and submitting the mixture to distillation, the iodine being retained in a solution of potassic iodide, which was afterwards titrated with a standard solution of sodic hyposulphite, starch being used as an indicator.

(*a.*) 1·6908 gram Pb-salt gave a solution of I in KI, which required 54·5 c.c. of a solution of hyposulphite, of which 1 c.c. was equivalent to 0·1343 gram iodine. Hence 0·731935 gram iodine had sublimed over, or the compound contains 43·28 per cent.

(*b.*) 0·57 gram gave a solution which required 18·45 c.c. of the above hypo-solution, equivalent to 0·2477835 gram iodine, or 43·47 per cent.

The iodine contained in the salt, which was free to act upon starch, was estimated by dissolving known weights of the dry crystals in strong cold solution of acetate of ammonium, and titrating with standard hyposulphite.

(*a.*) 0·5397 gram, dissolved in aqueous acetate of ammonia, required 10·2 c.c. of hyposulphite solution, of which 1 c.c. = 0·01343 gram iodine. This is equivalent to 0·136986 gram iodine, or 25·38 per cent.

(*b.*) 0·2442 gram required 4·65 c.c. = 0·0624495 gram iodine, or 25·57 per cent.

Sulphates of Potassium and Lead.

The potassium and lead contained in the salt were determined together by first gently igniting a known weight of the crystals, to expel the iodine in excess over PbI_2 and KI, and to diminish subsequent loss by spirting; and afterwards adding excess of dilute sulphuric acid and evaporating to dryness, the residue being carefully weighed.

(*a.*) 0·531 gram gave 0·316 gram of mixed sulphates, or 59·51 per cent.

(*b.*) 0·789 gram gave 0·469 gram of mixed sulphates, or 59·44 per cent.

The mean of the determination of K and Pb separately requires 58·987 per cent.

The empirical formula deduced from these analyses is

$$Pb_8C_{36}H_{54}O_{28}K_6I_{17}.$$

			Required.	Found.	
Pb_8	=	1656	33·229	33·195	33·249, 33·14
C_{36}	=	432	8·669	8·630	8·67, 8·59
H_{54}	=	54	1·083	1·106	1·112, 1·1
O_{28}	=	448	8·990	9·031	by difference.
K_6	=	234·6	4·707	4·668	4·69, 4·646
I_{17}	=	2159	43·322	43·370	43·47, 43·28
		4983·6	100·000	100·000	

	Required.	Found.	
Free iodine (assuming that the salt contains $5KI_3$)	25·43	25·46	25·55, 25·38
$PbSO_4$	48·633	48·59	48·67, 48·51
Mixed sulphates	59·119	59·47	59·44, 59·51
K_2SO_4	10·486	10·398	10·446, 10·35

The formation of a *rational formula* has at present baffled all my endeavours.

XXII. *On Certain Bismuth Compounds.* Part VII.

By M. M. Pattison Muir, F.R.S.E., Prælector in Chemistry, Caius College, Cambridge.

1. In the sixth part of these investigations I have pointed out one or two points of analogy and difference between the trichlorides of bismuth and phosphorus (*Chem. Soc. Jour.*, 1877, ii, 136). The former is less completely oxidised than the latter, when acted upon by air or by nitrogen trioxide, the chloride being in the state of fusion.

Michaelis (*Jenaische Zeitschr.*, vi, 239, vii, 110) has shown that at high temperatures phosphorus trichloride is capable of decomposing

very stable compounds; in these decompositions the trichloride acts as a reducing agent. I have examined the action of bismuth trichloride upon a few of those substances, the action of which upon the corresponding phosphorus chloride was investigated by Michaelis.

Sulphur chloride and phosphorus trichloride, when heated in sealed tubes to 160°, are decomposed in accordance with the reaction,

$$S_2Cl_2 + 3PCl_3 = PCl_5 + 2PSCl_3.$$

A quantity of sulphur chloride was heated in a sealed tube with excess of bismuth trichloride for 10 hours at 170 to 175°. The tube then contained crystals of separated sulphur; the bismuth trichloride remained altogether unacted upon.

According to Michaelis, the reaction $3PCl_3 + SO_2 = 2POCl_3 + PSCl_3$ takes place when sulphur dioxide and phosphorus trichloride are passed through a red-hot tube.

Bismuth trichloride was heated over a Bunsen lamp in a current of dry sulphur dioxide; the greater part of the trichloride was quickly volatilised and deposited again in the cold portion of the tube; the sublimate consisted of pure bismuth trichloride; the residue in the boat presented the appearance and possessed the properties of the oxychloride described in Part VI of these papers (*Chem. Soc. Journ.*, 1877, ii, 136). Estimation of chlorine showed that the residue, the amount of which was small compared with the weight of trichloride used, really consisted of this oxychloride. An experiment, in which sulphur dioxide and vapour of bismuth trichloride were passed through a red-hot tube, gave the same results.

Chromyl dichloride and phosphorus trichloride react very energetically upon one another.

Michaelis gives the equation $4CrO_2Cl_2 + 6PCl_3 = 2Cr_2Cl_6 + PCl_5 + 3POCl_3 + P_2O_5$, as expressing the results of this reaction.

When bismuth trichloride and chromyl dichloride are mixed, no action takes place; on warming the mixture, the bismuth salt gradually dissolves. When the dark-red liquid is left for some days over sulphuric acid, the chromyl dichloride is gradually absorbed by the acid, and a dark-red semi-solid mass is produced, which continues to evolve vapours of the dichloride, to a greater or less extent, for a long time. If exposed to the air, this dark-coloured mass quickly deliquesces, with production of bismuthyl chloride (BiOCl) and a solution containing chromic and hydrochloric acids, but entirely free from bismuth. The same decomposition is more quickly brought about by the addition of water to the semi-solid mass. Ether dissolves out a small quantity of bismuth trichloride from this mass; the solution is free from chromium. Absolute alcohol causes the production of a green liquid containing chromium and chlorine, but free

from bismuth. These reactions, I think, show that no chemical action has taken place between the bismuth and chromyl chlorides, but that the substance obtained is merely a solution of the bismuth salt in chromyl dichloride.

2. These reactions are in keeping with the facts that bismuthous chloride is less completely oxidised, under similar conditions, than the corresponding phosphorus compound; and that no bismuthic chloride analogous to phosphoric chloride (PCl_5) exists.

3. In a paper lately communicated to the Society (p. 170 of this volume) I have described a process for determining bismuth volumetrically, based upon the production of an oxalate having the formula, $Bi_2C_4O_9$. This oxalate is produced by boiling the normal oxalate, $Bi_2C_6O_{12}$, with water.

Souchay and Lenssen (*Ann. Chem. Pharm.*, cv, 245) have described normal bismuth oxalate as a salt containing $7\frac{1}{2}$ molecules of water, $6\frac{1}{2}$ of which are given up by heating to 100.° In *Watts's Dictionary* (vol. iv, p. 253), the formula of this salt is given as $Bi_2C_6O_{12}.15H_2O$: this is evidently a mistake. In the old notation the formula was $Bi_2C_{12}O_{24}.15HO$, which in the new becomes $Bi_2C_6O_{12}.7\frac{1}{2}H_2O$.

According to Souchay and Lenssen, the salt loses 14·3 per cent. of its weight when heated to 100°.

A quantity of bismuth oxalate was prepared by precipitating a slightly acid solution of bismuth nitrate with excess of a saturated solution of oxalic acid. The precipitate was washed with a very dilute solution of oxalic acid, dried by long-continued pressure between porous paper, and analysed.

The oxalic acid was determined by titration with standard permanganate; water was determined by heating in an air-bath, and bismuth by difference.

(1.) 0·471 gram required 67·2 c.c. permanganate = 0·1565 gram C_2O_4.

(2.) 0·659 gram required 95·1 c.c. permanganate = 0·2215 gram C_2O_4.

(3.) 1·363 grams lost 0·1745 gram after $5\frac{1}{2}$ hours' drying at 100°.

1 c.c. permanganate = 2·329 mgm. C_2O_4.

	Calculated for		Found.		
	$Bi_2C_2O_4.6H_2O$.	$Bi_2C_2O_4.7\frac{1}{2}H_2O$.	I.	II.	III.
C_2O_4.....	33·33	32·23	33·23	33·61	—
Bismuth....	53·03	51·29	53·77		—
Water.....	13·64	16·48	—	—	12·81

When the oxalate was heated to 130° for an hour, the color

changed to reddish-violet, the total loss amounting to 14·09 per cent. After $3\frac{1}{2}$ hours at the same temperature, the loss amounted to 14·38 per cent., the violet colour having become considerably deeper. At 150° decomposition proceeded with greater rapidity.

These results are more in keeping with the formula containing 6 molecules of water than with that given by Souchay and Lenssen, which requires $7\frac{1}{2}$ molecules. The water is evidently driven off at a temperature of 110° or so; and at a point not much above this, if one may judge from the change in the colour of the salt, decomposition begins. The chemists already quoted state that bismuth oxalate is decomposed at temperatures above 100°, with production of an acid oxalate and hypobismuthous oxide (Bi_2O_2). I heated a quantity of the oxalate, prepared as already described, in a closed crucible over a low Bunsen flame; the salt became black, and then began to assume a yellow colour; the heating was stopped; the residue washed with hydrochloric acid and exposed in a moist state to the air for several hours; no trace of the white hydrate which is produced by the oxidation, under similar conditions, of hypobismuthous oxide, was obtained. Examined under the lens, the residue was seen to consist largely of metallic bismuth; on heating, it was slowly converted into bismuthous oxide. The hydrochloric acid washings showed no traces of oxalic acid. It would thus appear that at a temperature considerably below redness bismuth oxalate is decomposed in a closed crucible, the oxalic acid being destroyed, and metallic bismuth being produced by the reducing action of the carbon particles, and perhaps also by carbon monoxide given off from the decomposing salt.

4. Souchay and Lenssen (*loc. cit.*) have described a basic oxalate of bismuth produced by boiling the normal oxalate with water until the supernatant liquid ceases to exhibit an acid reaction. To the oxalate thus obtained these chemists have assigned a formula which, translated into the new notation, becomes $Bi_2C_4O_9.H_2O$. Heintz (*Pogg. Ann.*, lxiii, 90) has examined the same salt and assigned to it the formula $Bi_2C_4O_9.1\frac{1}{2}H_2O$. According to Souchay and Lenssen this oxalate loses no water at 100°, but begins to decompose at 132°. According to Heintz, decomposition begins at 200° to 210°, and is attended with evolution of carbon dioxide only.

I prepared a quantity of the salt in accordance with the method already quoted. The analysis was conducted by dissolving in dilute hydrochloric acid, and titrating with standard permanganate solution.

1. 0·833 gram required 104·5 c.c. permanganate = 0·24338 gram C_2O_4 = 0·5808 gram Bi.

2. 0·6805 gram required 84·4 c.c. permanganate = 0·19657 gram C_2O_4 = 0·4691 gram Bi.

1 c.c. permanganate = 2·329 mgm. C_2O_4.

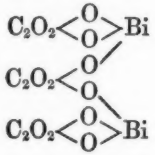
	Calculated for			Found.		
	$Bi_2C_4O_9$.	$Bi_2C_4O_9.H_2O$.	$Bi_2C_4O_9.1\frac{1}{2}H_2O$.	I.	II.	Mean.
C_2O_4.....	28·76	27·94	27·55	29·22	28·89	29·05
Bismuth ..	68·63	66·66	65·73	69·72	68·93	69·32
Water	—	2·86	4·23	—	—	—

In the foregoing analyses the bismuth was determined from the results of the titration with permanganate; whatever be the amount of water in the salt, the relation between C_2O_4 and Bi remains unaltered. Inasmuch as C_2O_4 corresponds with Bi, it is easy to calculate the permanganate in terms of bismuth after it has been standardised against oxalic acid or an oxalate.

0·849 gram was dried at 100° for some hours, but without suffering any diminution in weight. Dried for $1\frac{1}{2}$ hours at 150°, the salt was slightly blackened, and lost 0·007 gram = 0·83 per cent. After a second hour the loss amounted to 0·008 gram = 0·94 per cent., the salt being rather more blackened than before. After an additional hour at 185—190°, the salt became dark brown throughout, and lost 0·019 gram = 2·24 per cent. When heated over a Bunsen lamp, the oxalate was gradually converted into bismuthous oxide. These numbers certainly agree best with the supposition that this oxalate contains no water of crystallisation. At that temperature at which it begins to lose weight, it also begins to undergo decomposition.

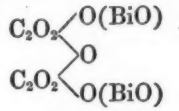
5. The properties of the two oxalates of bismuth, so far as the action upon them of acids and other reagents is concerned, have been detailed by Souchay and Lenssen with tolerable fulness. I find that, by mere contact with cold water, the normal is slowly converted into the basic oxalate.

6. The two oxalates of bismuth may be regarded either as derived from oxalic acid or from two of the hydrates of bismuth. From the former point of view the salt described in par. 3 is regarded as three molecules of oxalic acid, in which the whole of the hydrogen has been replaced by bismuth—

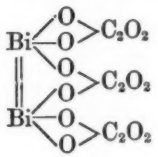


The basic salt is derived from two molecules of oxalic acid in which two hydroxyl groups are replaced by oxygen, that is to say, from an acid which bears exactly the same relation to oxalic acid that dichromic does to chromic acid, or pyrosulphuric to sulphuric acid. By repla-

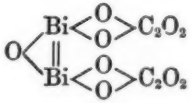
cing the whole of the hydrogen in this *dioxalic acid* by bismuthyl (BiO) we shall have the bismuth salt $(BiO)_2C_4O_7$—



If the oxalates be regarded as derivatives of bismuth hydrates, the normal salt will be obtained from the hydrate $Bi_2(OH)_6$ by replacing the hydrogen entirely by the group C_2O_2, thus—



while the basic salt will be obtained from the hydrate $Bi_2O(OH)_4$ by a similar replacement, thus—



From whichever point of view these oxalates are regarded, the basic salt is completely analogous to Löwe's dichromate of bismuth (see *Chem. Soc. Jour.*, 1876, ii, 19; and 1877, i, 649—651).

The normal salt must obviously be called bismuth oxalate; for the basic salt I would propose the name of *bismuthyl dioxalate*. The corresponding antimonyl dioxalate has been described by Souchay and Lenssen.

7. I have already described several attempts which I have made to prepare salts of the so-called bismuthic acid ($Bi_2O_5.H_2O$).

In one of the oldest papers upon bismuth salts, the preparation of three so-called bismuthates of potassium is detailed. Jacquelain (*J. pr. Chem.*, xiv, 1), in the year 1838, described experiments which resulted in the production of three salts, to which he assigned the formulæ (new notation) $2Bi_4O_7.K_2O$; $4Bi_2O_4.K_2O$; and $7Bi_2O_4.2K_2O$ respectively. I have again carried out two of the experiments made by Jacquelain exactly in the manner described by him.

A quantity of caustic potash was fused in a silver crucible, and bismuthous oxide was thrown in small successive quantities into the molten mass. The oxide dissolved very readily, the liquid becoming first greenish-yellow, then yellow-brown, and finally dark red-brown. The latter colour was attained when a considerable amount of bismuthous oxide had been added, and when the whole had been strongly

heated for 10 or 15 minutes. These observations are entirely in keeping with those made by Jacquelain. On allowing the fused mass to cool, a black solid was obtained, which appeared under a lens as a non-homogeneous mass containing grey or greyish specks. Jacquelain describes the fused mass as presenting the appearance of aventurin, and as containing quantities of crystals. I have repeated the experiment several times, and each time have obtained a similar result.

The black mass is very deliquescent; it is readily acted upon by water, with production of a strongly alkaline solution containing no bismuth, and a brownish-red residue, which, when washed with cold water until the washings cease to turn red litmus blue, is entirely free from potassium. The black mass is slowly decomposed by alcohol, with production of a brownish residue and an alkaline liquid free from bismuth.

When thrown into fused potash, the black solid is very quickly dissolved. Jacquelain says that it is much more quickly dissolved than bismuthous oxide. I have not observed much difference between the solubilities of the two substances in fused potash, so far as can be judged by the eye alone.

The formula which Jacquelain assigns to the substance which he obtained by adding bismuthous oxide to fused potash is $2Bi_4O_7.K_2O$. The numbers obtained by Jacquelain agree tolerably well with this formula; they are as follow:—

		Calculated.	Found.
Bismuth	=	84·07	86·16
Oxygen	=	11·21	11·56
Potash	=	4·71	2·38

There is a considerable discrepancy between the amount of potash found and the amount calculated. Jacquelain's formula, moreover, does not appear at all a probable one. If it be adopted, we must regard the substance as composed of bismuthous and hypobismuthic oxides combined with potash $(Bi_2O_3.Bi_2O_4)_2.K_2O$. The substance obtained as already described comports itself towards reagents exactly as a mixture of bismuthous oxide with one of the higher oxides would be expected to do.

The two salts to which Jacquelain assigns the formulæ $4Bi_2O_4.K_2O$ and $7Bi_2O_4.2K_2O$ respectively, are prepared, according to him, by the action of chlorine upon caustic potash-solution holding bismuthous oxide in suspension. The second salt is produced when a strong potash-lye is employed. If the percentage composition of the two salts be calculated, it is found that the numbers are very nearly the same for both. Jacquelain's actual results for the second salt agree quite as well (indeed rather better) with the first, as with the second formula.

I have attempted to prepare the salt $4Bi_2O_4.K_2O$ by following exactly the directions given by Jacquelain, only employing bromine as oxidiser in place of chlorine, as the former is much easier to manipulate. The result was a dark puce-coloured heavy powder, which, after washing with cold water until the washings were no longer alkaline to test-paper, contained small quantities of potassium. On boiling this substance with water, the water again acquired an alkaline reaction, which reaction became more apparent the longer the boiling was continued. After being boiled with successive quantities of water until the latter ceased to exhibit an alkaline reaction, the substance was found to be perfectly free from potassium. On treating it with a little strong nitric acid, red bismuthic hydrate was produced.

These results, taken along with the fact—insisted on by Jacquelain—that in the fusion of bismuthous oxide with potash, an oxide higher than Bi_2O_3 is certainly produced, and continues to exist at temperatures above that at which either Bi_2O_4 or Bi_2O_5 is decomposed, can be best explained, it seems to me, by supposing that a loose combination of potash with Bi_2O_4 or Bi_2O_5 is actually produced, but that this combination is very readily decomposed. In the first instance washing with cold water seems to effect decomposition; in the second boiling water is necessary. I am aware that the expression "loose combination" is a bad one on account of its vagueness, but I do not know of a better.

The general result appears then to be that the higher hydrates of bismuth exhibit exceedingly feeble acid properties, so feeble as certainly not to entitle them to the name of acids. These oxides do not combine with acids to form salts: hence they occupy a neutral position between the more marked positive oxides on the one hand, and the negative oxides on the other.

8. I thought it might be possible to form sulphobismuthates. With this end in view, several experiments were carried out, but they have all led to negative results. The experiments were briefly as follows:—An attempt was made to produce a sulphide of bismuth higher than Bi_2S_3 by passing sulphuretted hydrogen through water holding bismuthic oxide (Bi_2O_5) in suspension. A dark red powder was produced, which contained only 1 per cent. of sulphur. Treatment with alkali removed the sulphur, leaving bismuthic oxide.

Another attempt to prepare a sulphide higher than bismuthous sulphide was made by fusing carbonate of potassium, sulphur, carbon, and bismuthous sulphide together. The result was potassium sulphide in addition to the material employed in the fusion.

Lastly, an attempt to prepare a salt of bismuthous sulphide by fusing metallic bismuth, potassium carbonate, and sulphur led only to the formation of bismuthous sulphide and potassium sulphide. The fused

mass, treated with water, yielded a solution free from bismuth, the residue, after washing with water, yielded a solution free from potassium. Schneider (*Zeitsch. f. Chem.* [2], v, 630) states that a soluble double sulphide, $K_2S.Bi_2S_3$, is formed by the foregoing process. I have altogether failed to produce such a compound.

9. I have carried out a few experiments with bismuthous iodide, which it may be well to record in this place. The iodide was prepared by the wet method (Rammelsberg, *Pogg. Ann.*, xlviii, 166, and Arppe, *Pogg. Ann.*, lxiv, 248), also by Schneider's dry method (*Pogg. Ann.*, xcix, 470), which consists in heating together a mixture of bismuthous sulphide and iodine.

Rammelsberg says that a solution of potassium iodide converts bismuthyl chloride (BiOCl) into bismuthous iodide, and that in the preparation of the latter salt it is therefore immaterial whether the solution of bismuth contain precipitated oxychloride or not. The second part of this remark I find to be perfectly correct, but there is an error in the first part.

Pure bismuthyl chloride (BiOCl) was digested at the ordinary temperature for several hours with a large excess of a solution of potassium iodide, but not a trace of bismuthous iodide was produced. The addition of a few drops of hydrochloric or nitric acid caused the formation of a yellow liquid, but still no solid bismuthous iodide was formed.

A solution of bismuth in excess of nitric acid was added to another portion of the oxychloride; the first few drops caused the production of a yellow liquid, the addition of a larger quantity produced a precipitate of bismuthous iodide. Hence it is evident that bismuthyl chloride is not decomposed by potassium iodide solution. The addition of excess of potassium iodide solution to a mixture of bismuth chloride, bismuth oxychloride, and hydrochloric acid probably first causes the conversion of the dissolved bismuth into iodide, which is at once for the most part precipitated, with simultaneous production of potassium chloride. As potassium chloride is an easily soluble salt, a portion of the hydrochloric acid previously employed in holding the bismuth in solution will be free to dissolve fresh portions of bismuth by acting on the oxychloride present; the bismuth thus dissolved will be at once converted into iodide, and as such removed from the sphere of action; and these processes will continue until the whole of the bismuth is precipitated in the form of iodide. In keeping with this explanation is the fact which I have noticed, that if a small quantity of potassium iodide solution be added to a somewhat large quantity of bismuthyl chloride, and a few drops of hydrochloric acid be then poured on the mixture, the bismuth is slowly converted into iodide.

There appear to be some discrepancies in the accounts given of the action of water upon bismuthous iodide. I find that the iodide produced

by precipitation is decomposed with tolerable facility by cold water with production of the red oxyiodide, BiOI. The complete decomposition requires the agitation for some minutes of the precipitated iodide with three or four successive quantities of water. If hot water be employed, the decomposition is very much hastened. The iodide produced by subliming a mixture of bismuthous sulphide and iodine is decomposed by cold water only very partially, and only after prolonged contact; even when boiled with water the decomposition of the iodide is very slow. Bismuthous iodide is therefore a much more stable salt than either the corresponding chloride or bromide. When heated in a closed crucible, the iodide is for the most part sublimed unchanged, but a small quantity of the oxyiodide, BiOI, is produced, as noticed by Schneider (*J. pr. Chem.*, lxxiv, 424). In this respect the iodide differs from the other haloid bismuth compounds. In a paper communicated to the Society ("On Certain Bismuth Compounds," Part VI, *Chem. Soc. J.*, 1877, ii, p. 137) I have compared the oxidising action of air upon fused bismuthous chloride with the action upon fused bismuthous bromide. In the case of the latter salt the oxidation is carried further than in the case of the former. The iodide is, however, oxidised much more slowly than either the chloride or bromide.

Hydrochloric acid, it is stated, dissolves bismuthyl iodide (BiOI) readily; nitric acid causes the production of free iodine, while the bismuth goes into solution. I find that the addition of a very small quantity of hydrochloric acid to bismuthyl iodide brings about the production of bismuthous iodide, which is for the most part precipitated, and bismuthous chloride, which goes into solution. The addition of a few drops of sulphuric acid also causes the production of bismuthous iodide and a liquid holding bismuth in solution. Nitric acid when added in very small quantity exerts a similar reaction, but the bismuthous iodide produced is very quickly decomposed, with solution of bismuth and separation of iodine.

I also find that hydriodic acid acts slowly upon bismuthyl chloride, with production of bismuthous iodide. The two following equations in all probability represent the production of bismuthous iodide from the oxyiodide and oxychloride respectively:—

$$3BiOI + 6HCl = 2BiCl_3 + BiI_3 + 3H_2O.$$
$$3BiOCl + 6HI = 2BiI_3 + BiCl_3 + 3H_2O.$$

Just as potassium iodide solution is without action upon bismuthyl chloride, so is potassium chloride solution without action upon bismuthyl iodide.

XXIII.—*On Aromatic Nitrosamines.*

By Otto N. Witt, Ph.D.

In 1864 Griess published in the Philosophical Transactions his great paper on the diazo-compounds, in which he so thoroughly described the action of nitrous acid on primary aromatic amines that subsequent research has brought to light no new facts of importance.

In 1874 I made a few experiments on the action of nitrous acid, and especially its ethers, on *secondary* and *tertiary* amines, and was astonished to find that very beautiful substances were formed in these reactions. A few weeks after I had communicated my results to the Chemical Society of Zurich, Baeyer and Caro published their paper on nitrosodimethylaniline, the final product of the action of amylic nitrite on dimethylaniline; I have therefore in my research confined myself to the action of nitrous acid and its salts on *secondary* amines. The facts observed are shortly recorded in the *Berichte* of the Berlin Chemical Society; and a detailed account of the formation and properties of diphenylnitrosamine has been given in my inaugural dissertation. Since the publication of the latter, in 1875, I have studied more carefully some complicated reactions of diphenylnitrosamine, and the object of this paper is to bring before the Society a description of the phenomena observed, of the new substances prepared, and a short statement of my theoretical views on the subject.

Whenever a secondary amine is acted upon by nitrous acid, water and a nitrosamine are formed. The term "nitrosamine" I apply to any substituted ammonia which contains, instead of at least one atom of hydrogen, the univalent nitrosyl group, —NO, in immediate connection with the ammoniacal nitrogen. Thus the action of nitrous acid on diethylamine forms diethylnitrosamine—

$$\begin{matrix} C_2H_5 \\ | \\ NH \\ | \\ C_2H_5 \end{matrix} + NO.OH = H_2O + \begin{matrix} C_2H_5 \\ | \\ N.NO \\ | \\ C_2H_5 \end{matrix};$$

whilst diphenylnitrosamine is obtained by bringing diphenylamine into contact with ethylic or amylic nitrite—

$$\begin{matrix} C_6H_5 \\ | \\ NH \\ | \\ C_6H_5 \end{matrix} + NO.OC_2H_5 = \begin{matrix} C_6H_5 \\ | \\ N.NO \\ | \\ C_6H_5 \end{matrix} + C_2H_5.OH,$$

or by the action of nitrous vapours on diphenylamine, or of metallic nitrites on the hydrochloride of diphenylamine.

Diphenylnitrosamine is a substance remarkable for its great power of crystallisation. It can be easily obtained in large honey-coloured monoclinic crystals, melting at 66·5°, easily soluble in alcohol, benzene, and similar solvents, and giving a striking reaction with concentrated sulphuric acid, in which it rapidly dissolves, imparting to it a beautiful blue coloration, large quantities of pure nitric oxide gas being given off. Powerful reducing agents cause the formation of ammonia and reproduction of diphenylamine; but by careful reduction it may be converted into diphenylhydrazine, one of a beautiful series of new bases recently discovered by Emil Fischer. The action of aniline, or any other primary monamine, on diphenylnitrosamine is violent; if carefully controlled, however, the result is simple enough, being represented by the following equation:—

$$\begin{array}{l} C_6H_5 \\ | \\ N.NO \\ | \\ C_6H_5 \end{array} + 2(NH_2.C_6H_5) = \begin{array}{l} C_6H_5 \\ | \\ NH \\ | \\ C_6H_5 \end{array} + \begin{array}{l} C_6H_5 \\ | \\ N \\ \| \\ N \\ | \\ NH \\ | \\ C_6H_5 \end{array} + H_2O.$$

A corresponding amount of diphenylamine is regenerated, whilst the nitroso-group is employed in the formation of diazobenzene, which immediately combines with another molecule of aniline, forming diazoamidobenzene. The latter then undergoes the usual transformation into amidoazobenzene. Under certain circumstances a secondary reaction takes place, giving rise to a beautiful substance of the formula $C_{36}H_{29}N_5$, which is remarkable for a peculiar reaction. If heated with concentrated sulphuric acid to the boiling point of the latter, a fine blue colouring-matter is obtained, possessing a beautiful crimson fluorescence and a characteristic absorption spectrum with three dark bands.

If, instead of pure ethylic or amylic nitrite, the ordinary product obtained by leading nitrous vapours into ethylic alcohol be employed in the preparation of diphenylnitrosamine, or if nitrous vapours be introduced into a solution of diphenylamine, the products obtained differ greatly from diphenylnitrosamine, and a few experiments suffice to prove that they are mixtures of different substances in varying proportions. Their separation is, however, a matter of extreme difficulty: for gradual decomposition sets in if repeated recrystallisation is resorted to, and it was not until I found a means of preparing each of the different substances, independently and separately, that I could

attempt a successful inquiry into their constitution. Here I encountered another serious difficulty: all these substances, when subjected to organic analysis, suddenly give off large quantities of nitrous vapours; and this takes place so rapidly that even the use of a number of spirals of metallic copper does not always completely decompose the gas. On the other hand, the introduction of a large amount of metallic copper is detrimental to the accuracy of the analysis, as recently pointed out by Lietzenmayer (*Ber.*, xi, 306). When the nitrous vapours are given off a peculiar kind of very dense charcoal remains behind, the final combustion of which can be accomplished only by the prolonged passage of oxygen through the tube. Owing to all these difficulties my analytical data are scarcely within such close limits as I could have wished, although I have made quite an unusual number of combustions with the greatest care and by methods which, from long experience, I know to be perfectly trustworthy. On the other hand, I have in almost all cases determined not only carbon and hydrogen, but also nitrogen by the volumetric method.

It will be easily understood that analyses attended with such serious difficulties could not suffice to clear up the nature of my new substances, and I therefore had recourse to a closer study of their mode of formation. I soon found that ordinary ethylic nitrite contains invariably large quantities of nitric acid, the presence of which was easily accounted for, when I convinced myself that none of the methods employed for the production of what is commonly called nitrous anhydride, N_2O_3, produce this compound; and that by far the larger portion of the product obtained by the action of nitric acid of different strengths on either arsenious anhydride, or starch, or treacle, is nitric tetroxide, N_2O_4, which may be regarded as a mixed anhydride of nitric and nitrous acid. In contact with water or alcohol it furnishes both nitrite and nitrate, and this accounts for the invariable presence of nitric acid in all nitrous ethers prepared by the introduction of nitrous vapours into the corresponding alcohol. The nitric acid present proved also to be the cause of the peculiar difference between the action of pure and ordinary ethylic nitrite on diphenylamine.

This conclusion arrived at, I completely abandoned the use of ordinary nitrite, and with the purpose of obtaining a thorough insight into my experiments only employed mixtures of known quantities of pure amylic nitrite and nitric acid; acting with this reagent upon weighed quantities of diphenylamine and moderating or accelerating the reaction by the use of various solvents.

If 20 grams of finely powdered diphenylamine be placed in a dry flask and a mixture of

15 c.c. of nitric acid, sp. gr. 1·424,
35 grams of pure amylic nitrite,
100 c.c. of methylated alcohol,

be poured upon it, the diphenylamine dissolves instantaneously with a dark coloration, and a rise of temperature is perceptible; the flask is kept in constant motion, and the reaction, if necessary, accelerated by gentle heating. Suddenly crystals begin to settle out; and if the flask be now placed in iced water, a beautifully crystalline deposit is obtained. When crystals cease to form, the precipitate is filtered off and carefully washed with spirit, dried and recrystallised from chloroform. It forms beautiful plates of light yellow colour fusible at 133·5°, easily soluble in chloroform, benzene, hot alcohol, and glacial acetic acid.

The analytical data obtained with this substance are the following:—

	I.	II.	III.	IV.	V.	VI.	VII.
C...	59·90	59·70	59·84	60·03	59·60	—	—
H ..	4·20	4·30	4·30	4·40	4·40	—	—
N...	—	—	—	—	—	18·60	18·10
O...	—	—	—	—	—	—	—

This substance may easily be recognised as a nitrosamine; for it imparts a fine violet coloration to pure concentrated sulphuric acid, at the same time giving off nitric oxide gas. Now as the three available atomicities of the nitrogen in diphenylamine are thus proved to be engaged in a manner identical with diphenylnitrosamine, the only possible conclusion was, that some substitution had taken place in one or both of the two phenyl groups of the diphenylnitrosamine, and that the new substance was the nitrosamine of a substituted diphenylamine. We possess, as I have shown before, a means of regenerating the secondary amine from a nitrosamine by the action of aniline, which was resorted to and proved to be effectual; and equally good results were obtained by splitting off the nitroso-group by means of alcoholic potash. Whichever process was applied, it resulted in the formation of a new substance crystallising from dilute alcohol in small glistening scales of a pale yellow colour, melting at 132°. This substance does not colour sulphuric acid, but it dissolves with a fine red colour in alcoholic potash; subjected to organic analysis it proved to be mononitrodiphenylamine:—

	Theory for $C_6H_5.NH.C_6H_4.NO_2$.	Experiment. I.	II.
C.....	67·20	67·20	67·32
H.....	4·66	5·06	5·55
N.....	13·09	—	—
O.....	14·95	—	—
	99·90		

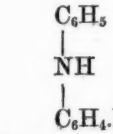
The product, from which this mononitrodiphenylamine was obtained, is therefore mononitrodiphenylnitrosamine; the following numbers—

C	59·30
H	3·70
N	17·30
O	19·70
$C_6H_5.N.NO.C_6H_4.NO_2$ =	100·00

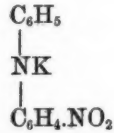
indicated for this substance by theory agree as closely with the results actually obtained as can be expected under the difficulties which the analysis of these substances offers.

Mononitrodiphenylnitrosamine, when dissolved in glacial acetic acid and subjected to the action of bromine, yields a precipitate of a canary-yellow colour, which is easily soluble in benzene and crystallises from this solvent in long silky needles fusible at 208·5—209°. If this substance be again treated with bromine, and heated with it for some time on the water-bath, another product is formed crystallising from benzene, in which it is not so easily soluble as the first product, in heavy, well-shaped small prisms, melting at 214·5—215°.

Mononitrodiphenylamine is a colouring matter, though a very weak one. Silk may be dyed yellow in its solution. The colouring properties of this substance are due to the entrance of a nitro-group into diphenylamine, which at the same time renders the imido-hydrogen replaceable by metals—



Mononitrodiphenylamine.



Potassium mononitrodiphenylamine.

But as soon as the imido-hydrogen is replaced by the nitroso-group, the colouring properties of the compound are destroyed, the influence of the nitro-group being paralysed. This may be easily demonstrated by introducing mononitrodiphenylnitrosamine into a very cold solution of potash in alcohol. In the first instance no coloration is observed. But on heating, or even on standing for a short time, a dark scarlet coloration appears, due to the elimination of the nitroso-group and the formation of mononitrodiphenylamine, which, as already observed, is a colouring matter.

If the proportions of nitric acid and amylic nitrite be altered, and the spirit be exchanged partly or entirely for another solvent, which

expedites the reaction, more nitro-groups may be introduced into the molecule of diphenylnitrosamine. The following method has been found to give satisfactory results.

17 grams of diphenylamine are introduced into a dry flask surrounded by iced water. Then a mixture of—

50 c.c. of glacial acetic acid,
40 c.c. of nitric acid, 1·424,
50 c.c. methylated spirit,
48 grams nitrite of amyl,

is added all at once. The diphenylamine dissolves with a dark colour, and very soon small granular crystalline aggregates begin to settle out. When the precipitate no longer increases, it is filtered off on the filter-pump, the mother-liquor is carefully removed, and the precipitate washed with spirit and finally with ether. It is then dried at the ordinary temperature, and appears, when dry, as a sandy powder of light yellow colour. Recrystallisation may be effected from chloroform, in which the new compound is but sparingly soluble, but I have not been able to detect any difference in the analytical results obtained with either the recrystallised or the crude product. Their behaviour with reagents and their characteristic appearance are also very much the same. The reaction of this body with sulphuric acid, in which it dissolves with a dirty violet coloration, giving off nitric oxide at the same time, proves it to be a nitrosamine. The analytical results, however, do not agree with any simple formula, but the numbers for at least the carbon and hydrogen are intermediate between those required for di- and for tri-nitrodiphenylnitrosamine—

	Theory for		Experiment.		
	$C_{12}H_8N_4O_5$.	$C_{12}H_7N_5O_7$.	Crude.	Recrystallised.	
			I.	II.	III.
C.....	50·00	43·25	46·95	—	47·01
H.....	2·75	2·10	3·99	—	3·18
N.....	19·45	21·05	—	19·04	—
O.....	27·80	33·60	—	—	—
	100·00	100·00			

I therefore concluded that the new substance, although apparently uniform and not separable by repeated recrystallisation, was contaminated with some impurity, and hoped to effect a more successful purification on removing the nitroso-group by means of alcoholic potash or aniline.

For this purpose 20 grams of the product were placed in a flask, together with 100 c.c. of spirit, and 50 c.c. of a 20 per cent. solution of potassic hydrate in alcohol. On heating, a splendid purple coloration

appeared, which gradually increased in intensity until all was dissolved. Dilute hydrochloric acid was now added until the colour had changed to a bright orange, and, finally, a large quantity of water was introduced; the precipitate was collected on a calico filter, washed carefully, pressed, and treated with about 400 c.c. of boiling methylic alcohol. The solution was filtered from the part which remained undissolved (A), and on cooling deposited crystals of an obviously impure product (B).

If aniline be employed for the removal of the nitroso-group, the following method may be adopted:—

20 grams of the new product,
30 grams of pure hydrochloride of aniline,
25 grams of aniline,
50 c.c. of spirit,

are heated for about half an hour on the water-bath. Plenty of dilute hydrochloric acid is then added, and the precipitate boiled out three successive times with extremely dilute nitric acid. All the amidoazobenzene is thus removed, and may be found in the extract. What remains undissolved is treated with methylic alcohol as before, and the part insoluble in the boiling alcohol (A) treated separately from that which deposits on cooling (B).

The latter, B, is successively extracted with small quantities of boiling methylated spirit and glacial acetic acid, and both solutions removed by hot filtration. After this treatment the new substance requires one crystallisation from ethylic, or, better, isobutylic alcohol to be quite pure. It then forms long, thick, pointed needles of great brilliancy and lustre, of a dark yellow colour, with a slight bluish dichroism, fusible at 214°. They dissolve in alcoholic potash with a bright purple colour, which is destroyed by the addition of cold water, but reappears on boiling. Analysis proved them to be dinitrodiphenylamine:—

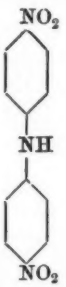
	Theory For $C_{12}H_9N_3O_4$.	Experiment. I.	II.	III.	IV.
C.....	55·60	56·50	54·90	56·39	—
H.....	3·50	4·80	4·09	4·07	—
N.....	16·20	—	—	—	16·64
O.....	24·70	—	—	—	—
	100·00				

The substance A, insoluble in methylic alcohol, was boiled out two or three times with this solvent, and then recrystallised from pure xylene. From this hydrocarbon it is deposited slowly in small, indistinct

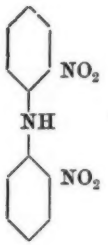
granular crystals of a vermillion colour, fusible at 211·5°. It dissolves in alcoholic potash with scarlet colour, and the solution behaves in a similar manner to the purple solution of the body first described. On analysing it I found that it was isomeric with the yellow substance, and corresponds also to the formula of dinitrodiphenylamine:—

	Theory For $C_{12}H_9N_3O_4$.	Experiment. I.	II.	III.	IV.
C.....	55·60	56·80	56·52	—	—
H.....	3·50	4·25	4·17	—	—
N.....	16·20	—	—	17·00	16·29
O.....	24·70	—	—	—	—
	100·00				

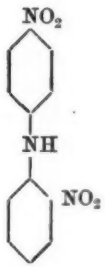
This fact is by no means surprising. If we suppose that, in the dinitrodiphenylamines obtainable by direct nitration, the two nitro-groups enter two different phenyl-groups, there are still three different substances likely to arise:—



Diparanitro-diphenylamine.



Diorthonitro-diphenylamine.



Orthoparanitro-diphenylamine.

The meta-position is out of the question, as a nitro-group entering into an aromatic molecule never occupies a meta-position to a basic group already present. The two dinitrodiphenylamines here described most likely correspond to the first and third formulæ, for they both arise from further nitration of the same mononitrodiphenylamine, which, in all probability contains its one nitro-group in the para-position.

All the substances hitherto described give, when treated with nitric acid of the highest concentration, hexanitrodiphenylamine, a substance originally discovered by E. Kopp, more closely investigated by Gnehm, and repeatedly introduced as an orange dye into commerce. On careful nitration diphenylnitrosamine gives, as I observed some time ago, and Gnehm recently published, tetranitrodiphenylamine. Thus diphenylamine, through the agency of its nitrosamine, allows of

the introduction of one nitro-group after the other up to six, with exception of three and five, into its molecule, and we now know, irrespectively of isomerides obtained with picric chloride and dinitrochlorobenzene by Clemm and P. T. Austen, the following nitro-derivatives of diphenylamine :—

Mononitrodiphenylamine, $C_{12}H_{10}N_2O_2$.

Dinitrodiphenylamine, $C_{12}H_9N_3O_4$ (two isomers).

Tetranitrodiphenylamine, $C_{12}H_7N_5O_8$.

Hexanitrodiphenylamine, $C_{12}H_5N_7O_{12}$.

I do not doubt that my new method of nitrating substances in dilute solutions with the aid of alkylic nitrites, will be found applicable in a great many cases, where nitration has hitherto offered unusual difficulties. It would also appear that this method furnishes some support to the theory already advanced, that the formation of nitroso-compounds always precedes the introduction of the nitro-group into the molecule of aromatic substances.

Thus far I have described as much of my research on the action of nitrous acid on secondary amines as has become fit for publication since my last communication to the *Berichte*. I should have preferred to wait until I could have given some account of the reduction-products of my new nitro-compounds, and investigated more closely their brominated derivatives, had it not been for an incident which made it desirable to publish without delay.

In February, Mr. Meldola communicated to the *Chemical News* a note on "A New Colouring-matter," and, at the same time, was good enough to send me two specimens of his preparations, one representing the substance arising from the action of nitric tetroxide on diphenylamine in an acetic acid solution, the other the product obtained from the first by the action of alcoholic potash. On closely examining and comparing our specimens, we found the first product to represent a mixture of the nitrosamines described in this paper, whilst the second was a mixture of the nitrated diphenylamines, which correspond to the nitroso-compounds. On ascertaining that the subjects of our investigations were identical, and that the action of nitrous acid on diphenylamine and other secondary amines had occupied me for several years, Mr. Meldola was kind enough to relinquish his claim to the continuation of this research, for which I have much pleasure in thanking him: at the same time I wish to point out that the practical application of mono- and di-nitrophenylamine as a dye-stuff, called citronine, is solely and entirely due to Mr. Meldola. The shades obtained on silk with citronine are truly magnificent, and no other artificial colour can compete with it as regards this particular tint; unfortunately, owing to the inefficiency of the nitro-group as a chromophor, and to the extreme weakness of the salt-forming groups in

citronine, it is not a strong colouring-matter, and this, combined with its insolubility in water, renders it of less general applicability than it otherwise deserves. Still, it is a very interesting fact, that in citronine an artificial colouring-matter has for the first time been found, which, if it were not for the little difficulties just mentioned, might with advantage replace turmeric and quercitron.

I have the intention of bringing before the Society, in a second paper, the results which I hope to obtain in the continuation of this research.

XXIV.—*On some New Derivatives of Anisoïl (Anisol).*

By W. H. Perkin, F.R.S.

A short time since I showed that methylparoxyphenyl-acrylic, -crotonic, and -angelic acids, when heated,—or, better, in the case of the two latter acids,—when converted into the hydrobromo-additive compounds, and then treated with sodium carbonate, yield para-derivatives of anisoïl. I have now extended my experiments to the corresponding ortho-acids, and obtained the following results.

Orthovinylanisoïl.

On boiling β-methylorthoxyphenylacrylic acid, it gradually decomposes, carbonic anhydride being given off, and an oil distilling over. This is purified by washing with dilute potassium hydrate and distillation with water; but with the view of obtaining it in a still purer state, it was thought desirable to see if an additive derivative of the acid could be formed, which would decompose when treated with an alkaline solution, and yield this body.

For this purpose dry precipitated methylorthoxyphenylacrylic acid was placed in contact with hydriodic acid, sp. gr. 1·94, for two or three days, the mixture being frequently agitated. The resulting product was drained from the excess of hydriodic acid by means of a filter-pump. It was found best not to wash it, as it is very unstable, and soon decomposes when in contact with water. It was then added in small quantities to a cold saturated solution of sodium carbonate, the mixture being well stirred and not allowed to get warm during the reaction, otherwise considerable quantities of a polymerised product are formed; this, however, sometimes happens even when great care is taken. The resulting milky fluid is then placed in a retort and boiled

until no more oily product distils over. The distillate is then warmed to promote the separation of the oil into a layer, which is then collected and dried with potassium carbonate. On analysis it gave the following numbers: —

·2158 of substance gave
·6364 of CO_2 and
·1438 of H_2O.

	Theory for $C_9H_{10}O$.	Experiment.
Carbon	80·59	80·42
Hydrogen	7·40	7·43

The formation of this substance, which I propose to call *orthovinylanisoïl*, may be written thus:—

I. $C_6H_4\left\{\begin{matrix}(OCH_3)^o\\CH{=}CH-CO(OH)\end{matrix}\right. = C_6H_4\left\{\begin{matrix}(OCH_3)^o\\CH{=}CH_2\end{matrix}\right. + CO_2.$

Methylorthoxyphenylacrylic acid. — Orthovinylanisoïl.

II. $C_6H_4\left\{\begin{matrix}(OCH_3)^o\\CH_2{-}CHI-CO(OH)\end{matrix}\right. = C_6H_4\left\{\begin{matrix}(OCH_3)^o\\CH{=}CH_2\end{matrix}\right. + CO_2 + HI.$

Hydriodomethylorthoxyphenylacrylic acid. — Orthovinylanisoïl.

Orthovinylanisoïl polymerises so quickly when heated, that its boiling point could not be determined with certainty, but it seems to be between 195° and 200° C. When heated to 150° for about an hour, it solidifies to a transparent glassy substance, which is easily soluble in benzene, but insoluble in alcohol. This solid product when heated strongly distils, orthovinylanisoïl being regenerated.

The odour of orthovinylanisoïl is very different from that of its isomeride, paravinylanisoïl, being somewhat similar to that of high-boiling coal-tar naphtha, but more fragrant and not so strong.

* Its specific gravity is—

at 15° 1·0095
at 30° 1·000

When agitated with bromine-water it decolorises the latter, forming a nearly solid product. Heated with dilute nitric acid, it changes to a yellowish-brown heavy oil, becoming quite thick on cooling; this product is partially soluble in aqueous potassium hydrate. With concentrated sulphuric acid it becomes solid and of a bright-red colour.

Orthallylanisoïl.

Methylorthoxyphenylcrotonic acid, when left in contact with hydrobromic acid, sp. gr. 1·74, for two or three days, combines with it; but the resulting acid, unlike the corresponding para-compound, when treated with an alkaline carbonate and then distilled, yields but a

* Compared with water at the same temperature.

small quantity of oily product; a large quantity of an uncrystallisable acid is, however, found in combination with the alkali; this is probably an oxy-acid. If, however, hydriodic acid, sp. gr. 1·94, be used in place of hydrobromic, the resulting acid yields a large quantity of an oil when treated with an alkaline carbonate or acetate. A specimen of this dried over potassium carbonate and then distilled gave, on analysis, the following numbers :—

I. ·1894 of substance gave
·5647 of CO_2 and
·1384 of H_2O.

II. ·2178 of substance gave
·6482 of CO_2 and
·1631 of H_2O.

	Theory for $C_{10}H_{12}O$.	Experiment. I.	II.
Carbon	81·08	81·3	81·17
Hydrogen	8·10	8·11	8·3

This substance I propose to call *orthallylanisoïl;* the formula may be expressed thus :—

$$C_6H_4\begin{cases}(OCH_3)^o\\CH_2—CHI—CH_2.CO(OH)\end{cases} = C_6H_4\begin{cases}(OCH_3)^o\\CH=CH—CH_3\end{cases} + HI + CO_2.$$

Hydriodomethylorthoxyphenylcrotonic acid. Orthallylanisoïl.

Orthallylanisoïl is a highly refracting liquid boiling without polymerising at 222—223° C. Its specific gravity is—

at 15° ·9972
at 30° ·9884
at 45° ·9793.

Its odour is similar to that of its vinylic homologue, but fainter. When cooled in a freezing mixture of snow and hydrochloric acid, it thickens but does not solidify.

It combines with bromine, forming a thick heavy oil. Cold nitric acid, sp. gr. 1·3, does not appear to act upon it in the cold, but on heating the mixture, red fumes are given off, and a brownish-yellow viscid oil, gradually solidifying to a resinous mass, results. With concentrated sulphuric acid it becomes solid and of a red colour ; but on addition of water, it changes to a white opaque product soluble in benzene.

Orthobutenylanisoïl.

Methylorthoxyphenylangelic acid, when treated with hydrobromic acid, combines with it, but the resulting compound yields only a very

small quantity of oily product when treated with an alkaline carbonate; but if hydriodic acid be employed, the yield of product is good. The specimen of oil analysed was distilled with water and dried over potassium carbonate.

·2083 of substance gave
·6228 of CO_2 and
·1634 of H_2O.

	Theory for $C_{11}H_{10}O$.	Experiment.
Carbon	81·48	81·54
Hydrogen	8·64	8·71

The formation of this substance, which I propose to call *orthobutenylanisoïl*, may be expressed thus :—

$$C_6H_4\begin{cases}(OCH_3)^o\\CH_2—CHI—CH_2—CH_2CO(OH)\end{cases} = C_6H_4\begin{cases}(OCH_3)^o\\CH=CH—CH_2—CH_3\end{cases} + HI + CO_2.$$

Hydriodomethylorthoxyphenylangelic acid. Orthobutenylanisoïl.

Orthobutenylanisoïl boils at 232—234° without polymerising.
Its specific gravity is—

at 15° ·9817
at 30° ·9740.

When cooled in snow and hydrochloric acid, it does not solidify, but becomes thick. Like its homologues it combines with bromine, and also becomes solid and of a red colour when treated with concentrated sulphuric acid, the product losing its colour when washed with water.

Boiled with dilute nitric acid it becomes yellow, but is only slowly acted upon. Strong nitric acid acts upon it with violence and dissolves it; water precipitates from this solution a brown resin, which is mostly soluble in aqueous potassium hydrate.

Paravinylanisoïl.

I mentioned in my paper, already referred to, that I endeavoured to produce paravinylanisoïl from methylparoxyphenylacrylic acid by treating it with hydrobromic acid, hoping to obtain an addition-product which would decompose with alkaline carbonates in the usual manner; but no result was obtained, as the methylparoxyphenylacrylic acid decomposed when brought in contact with hydrobromic acid. As, however, I have succeeded in obtaining orthovinylanisoïl by a modification of this process, viz., by substituting hydriodic for hydrobromic acid, I applied this form for the preparation of this body.

Dry precipitated methylparoxyphenylacrylic acid, when left in con-

tact with hydriodic acid, sp. gr. 1·94, for two or three days, combines with it, and the product, when drained from the excess of hydriodic acid and treated with an alkaline carbonate, yields the desired product. Unfortunately a good deal polymerises and becomes solid. The pure paravinylanisoïl, however, was easily separated from this by distillation with water.

Thus obtained, it differed but little from that prepared by the distillation of methylparoxyphenylacrylic acid; it was, however, somewhat purer, as its fusing point was higher, viz., +3° instead of —1°. Its specific gravity is—

at 15° 1·002
at 30° ·9956.

It will be, perhaps, worth while to notice in what respects the para- and ortho-derivatives of anisoïl I have obtained differ from each other. The difference in the boiling points appears to be about 10°.

Paravinylanisoïl	204—205°
Orthovinylanisoïl.....	uncertain
Parallylanisoïl	232°
Orthallylanisoïl.....	222—223°
Parabutenylanisoïl	242—245°
Orthobutenylanisoïl	232—234°

The density is also slightly higher in the ortho-derivatives.

	15°	30°	45°
Paravinylanisoïl	1·0029	·9956	—
Ortho „	1·0095	1·000	—
Parallylanisoïl	—	·9852	·9761
Ortho „	·9972	·9884	·9793
Parabutenylanisoïl	—	·9733	—
Ortho „	·9817	·9740	—

The ortho-compounds also refuse to crystallise, even when placed in a freezing mixture; the para-derivatives crystallise freely.

α-Methylorthoxyphenylacrylic acid obtained from coumarin, when treated with hydriodic acid and then with an alkaline carbonate, yields an oil which is apparently identical with the orthovinylanisoïl prepared from the β-acid. I am at present investigating this remarkable α-acid, and endeavouring to obtain some of its homologues.

XXV.—*Note on the Action of Ammonia on Anthrapurpurin.*

By W. H. Perkin, F.R.S.

In a paper on anthrapurpurin published in the Journal of this Society (vol. xxvi, p. 432), I mentioned that an ammoniacal solution of that colouring matter, when heated in a sealed tube to 100° C., changed in colour from purple to indigo-blue, hydrochloric acid throwing down from this solution a dark purple precipitate which redissolved in ammonia with a blue colour. This substance dyes alumina mordants a purple, and weak iron mordants an indigo-blue colour.

This substance I find is an unstable body easily convertible into anthrapurpurin. This is easily shown by acidifying a portion of the blue ammoniacal solution with hydrochloric acid; at first a precipitate is formed, which dissolves on heating, but after a short time the liquid becomes turbid, owing to the precipitation of anthrapurpurin. Also if strong aqueous potassium hydrate be added to the blue solution, it at first turns to a bright purple-red colour, but on boiling changes to a blue-violet, due to anthrapurpurin.

If instead of heating the sealed tubes containing an ammoniacal solution of anthrapurpurin to 100°, a temperature of 160—180° be employed, a purple solution results. On acidifying this with hydrochloric acid, a chocolate-coloured precipitate forms. This, when washed and boiled with a solution of barium hydrate, mostly dissolves, forming a purple solution. On acidifying this, a precipitate is formed which, after washing with water and drying, was digested with alcohol. The resulting dark red solution on being concentrated deposited the new body in crusts of a dark greenish or black colour, sometimes with a greenish metallic aspect, and only indistinctly crystalline. When powdered it is of a chocolate colour.

On analysis it gave the following numbers:—

I. ·286 of substance gave
·687 of CO_2 and
·095 of H_2O.

II. ·313 of substance gave
15 c.c of nitrogen. Temp. 22°. Bar. 754 mm.

	Theory for $C_{14}H_9NO_4$.	Experiment. I.	II.
Carbon	65·88	65·50	—
Hydrogen	3·53	3·65	—
Nitrogen	5·49	—	5·38

This substance may be called *anthrapurpuramide* or *amidoalizarin*, though it differs entirely from the amidoalizarin produced by the action of nascent hydrogen on nitroalizarin (*Journ. Chem. Soc.*, 1876, ii, 581). Its formation may be expressed thus—

$$C_{14}H_5O_2\begin{cases}OH\\OH\\OH\end{cases} + NH_3 = C_{14}H_5O_2\begin{cases}NH_2\\OH\\OH\end{cases} + OH_2.$$

Anthrapurpuramide is not very easily soluble in alcohol. The solution in this solvent is of a clear dark orange-red colour. It is nearly insoluble in water.

Solutions of the alkalis and alkaline earths dissolve it with a purple colour. Boiling solution of potassium hydrate does not decompose it. It does not dye mordants.

When nitrous acid is slowly passed through its boiling alcoholic solution, a brown precipitate separates. This, when collected and washed, dissolves in a solution of barium hydrate, forming a brownish-red solution. On filtering this, and adding hydrochloric acid, a precipitate is obtained, and this when washed and dissolved in hot glacial acetic acid, yields a brownish-yellow solution, which on standing deposits crystals of crude isoanthraflavic acid. I had not sufficient material to purify for analysis, but from the fact that it yields anthrapurpurin on fusion with potassium hydrate, there can be no doubt of its identity.

XXVI.—*Notes on the Tannins.*

By B. H. Paul, Ph.D., and C. T. Kingzett.

In a paper recently published by Mr. H. R. Proctor, he has shown that no two processes for the estimation of tannin give similar or comparable results, although when the same process is tried against products of the same nature, the results obtained by each process are tolerably constant, that is to say, cutch may be compared with cutch, mimosa with mimosa, and tannin with tannin, so long as the same process is employed; but even in this case tannin cannot be compared with cutch.

In the course of professional practice we have had occasion to examine various tanning materials, in such a way as to enable us, if possible, to value one kind of material against another; and, to make

a long story short, it may be said our results fully sustained Mr. Proctor's statements. We could compare cutch with cutch, but not with ordinary gallotannic acid, as it is called, and even when each kind of substance was re-examined by different processes, varying results were obtained. Thus a sample of tannic acid (sold as pure) showed with Gerland's antimonial process 76 per cent. of pure tannin; by the volumetric process, employing lead acetate and using potassium ferricyanide as an indicator, 179 per cent.; and by the indigo process it showed (using the figures worked out by Neubauer) 135 per cent. tannin, which figure, corrected for admixed gallic acid by the gelatin and salt treatment, became 93 per cent. real tannin.

A number of perfectly unmeaning results were therefore obtained, and the difficulty was made still greater when cutch and extract of mimosa bark were similarly compared.

Although the term "tannin" appears to indicate that the astringent character of different plants is due to the presence of a common substance, this supposition is not only erroneous to a large extent, but it becomes delusive when an attempt is made to base analytical methods upon it. The commercial value of different materials can so far be ascertained only by the practical tanner.

If the various kinds of tannin were all glucosides, it might be possible to arrive at some sort of valuation by determining the amount of glucose which they are capable of yielding. It was this idea that led to the experiments detailed in the paper.

Strecker stated that ordinary gallotannic acid (from gall-nuts) was a glucoside, splitting up when boiled with dilute acid as follows:—

$$C_{27}H_{22}O_{17} + 4H_2O = 3C_7H_6O_5 + C_6H_{12}O_6,$$

but H. Schiff has recently shown that tannic acid as ordinarily prepared is only digallic acid, splitting up thus, $C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$; and this view has been confirmed by Stenhouse in a study of the action of bromine upon tannin. Schiff, however, expresses the opinion that the unaltered natural tannin of gall-nuts may probably be a glucoside, not of gallic acid but of digallic acid, and that it is to some extent decomposed by the mode of preparation (comp. foot-note, *Ann. Chem. Pharm.*, clxx, 175). In that case its decomposition would be represented by the equation—

$$C_{34}H_{28}O_{22} + 2H_2O = C_6H_{12}O_6 + 2C_{14}H_{10}O_9.$$

These statements of Schiff led us to examine a number of commercial samples of tannin, by boiling them with dilute acids and examining the products for glucose. The solution thus obtained reduced Fehling's solution, although in every case it was found to be

quite free from sugar, and to contain only gallic acid. Moreover, the freedom of the original samples of tannin from any glucoside was shown by the fact that they gave no purple coloration with strong sulphuric acid alone, although when sugar was added the coloration came out strongly. This result is in accordance with the circumstance, mentioned by Schiff in a supplementary note to his paper, that tannic acid is now prepared commercially with dry ether, and not with ether containing water or with a mixture of ether and dilute alcohol. It seems, therefore, to be a matter of some doubt whether tannin is after all a glucoside even in its natural state, because if it were so, a process sufficient to effect its decomposition so far as to eliminate glucose, would scarcely stop at that stage, but would also presumably give gallic acid and not digallic acid.

As we could find nowhere any statements regarding the constituents of cutch and mimosa bark extract, further than that they both yield a peculiar acid named *mimotannic acid*, some experiments were made also with these materials.

Cutch of commerce is a hard, brownish-black, shining substance, prepared in India and elsewhere from the *Acacia Catechu*, and other trees.

The method of procedure employed in our experiments consisted in boiling cutch for a number of hours with a quantity of dilute sulphuric acid (2—5 per cent.). During this operation 5 per cent. of a dark brown insoluble matter forms, which appears to be an imperfectly changed substance, judging from its general characters and from the fact that it gives the reactions of a glucoside, only in a less degree than the original cutch. The sulphuric acid solution admits of treatment in two ways. It may be precipitated either by acetate of lead or by baryta-water, both of which reagents remove the same acid substance, and leave glucose of an unfermentable character in the filtrate. This glucose was estimated at 25 per cent. on the original cutch.

Mimosa bark is the product of the *Acacia mimosa*, and furnishes in part the cutch of commerce. Extracts made of this bark gave, by the processes just described, similar results, the sugar obtained being estimated at about 8 per cent. on the bark.

The peculiar acid removed by precipitation with acetate of lead or baryta-water deserves a few words. If lead be employed, the acid may be obtained by decomposition of the precipitate with sulphuretted hydrogen, and removal of the sulphuric acid from the concentrated filtrate by means of carbonate of barium or carbonate of lead.

If baryta-water be employed, it is best to decompose the precipitate with sulphuric acid, and then to remove the excess of acid from the filtrate in the same way.

The solution of organic acid thus obtained is of a faint red colour, and shows the following reactions :—

1. An intensified red colour on addition of ammonia.
2. A dark colour with ferric chloride, but only a trace of precipitate.
3. No appreciable reaction with ferrous sulphate.

But a solution rendered neutral with soda became much darker itself, and gave—

1. With ferric chloride a dark-coloured precipitate.
2. With ferrous sulphate a bluish-black precipitate.

It also gave precipitates with other reagents.

On evaporating a solution of the free acid, oxygen was evidently absorbed, and a dark brown matter deposited on the sides of the dish. In fact it was impossible to concentrate the solution or to work profitably with it any further. Without attempting to describe the characters of the insoluble matter formed during the boiling of cutch with sulphuric acid, the foregoing notes may be summarised as follows :—

1. The supposition that tannin, as it exists in gall-nuts, is a glucoside is rendered doubtful, and the sugar met with in some samples of tannic acid is more probably referable to an impurity, as Rochleder and Kawalier assumed. Schiff leans to the opinion that the tannin in gall-nuts is a glucoside, but he states that the gallotannic acid met with in commerce is not a glucoside, but digallic acid.

2. The astringent principle common to cutch and extract of mimosa bark is shown to be either a glucoside or associated with a substance of that nature, since they both yield unfermentable sugar, together with a peculiar acid distinct from gallic acid.

The specimen of sugar exhibited has been purified by redissolving in water, precipitation with ammoniacal lead acetate, and decomposition of the precipitate with sulphuretted hydrogen.

ANNIVERSARY MEETING,

March 30th, 1878.

Dr. Gladstone, F.R.S., President, in the Chair.

The following report was read by the President:—

The history of the Chemical Society during the past twelve months has been an eventful one. For some time previously proposals had been made for extending its functions beyond what had hitherto been contemplated; this gave rise to much serious deliberation, but about the commencement of last year, many circumstances combined to show that such considerable changes were either impracticable under the present charter, or undesirable; and the subsidence of the discussion left the Council free to devote their attention to various internal reforms. It is hoped that those changes, which have already been carried into execution, together with such as await their completion this evening, may help to consolidate the work of the Society. In the meanwhile the more strictly scientific part of the Society's operations has been steadily carried on; and the commencement of the actual benefits resulting from the establishment of the Research Fund, has given a special feature to this year's proceedings.

I propose to refer to these various points in some little detail.

At the last meeting my predecessor in this chair felt it his duty to lay before the members the serious difficulties that had arisen from the action of a section of the Fellows; the conversation that followed was advantageous by informing the Council of the views entertained by different gentlemen present, and the new Council set themselves at once to consider how far any of these objections might be recognised as real, and therefore might be remedied. Committees were nominated for revising the bye-laws; and for improving, if possible, the publication of the *Journal*. An extraordinary general meeting was called shortly afterwards on the requisition of several of the Vice-Presidents and other prominent Fellows of the Society. It took place on the 31st of May, and the statements which the Council laid before the meeting seemed to remove, in a great measure, if not entirely, any dissatisfaction that had previously existed.

The whole subject of the bye-laws has received the very careful attention of the Council, involving the expenditure of much time and

thought. The proposed modifications are now in the hands of the Fellows, and await their adoption, or otherwise, this evening. The verbal changes are numerous, but the real alterations affect mainly the mode of electing Fellows, and of appointing auditors.

There has been an entire alteration in the constitution of the Publication Committee. It was originally intended that leading members of the Society should revise the work of the abstractors: hence the committee was made a large one, so as to represent all the different sections into which chemical papers might be divided. It was soon found, however, that this was attended with great difficulties; and the duty of revision practically fell into the hands of the Editor. At the same time the very largeness of the Publication Committee lessened the feeling of responsibility in its individual members. It was therefore determined to reduce the number to the five officers of the Society, with six other members. The remuneration given to the abstractors was rendered more adequate to the services required of them; and additional rules were made for their guidance, with a view especially to brevity and uniformity in the expression of results of analysis and of formulæ.

A separate pagination has been adopted for the papers and for the abstracts, so that when bound up, the Society's work may appear in a continuous form.

Other regulations have been made for expediting the publication of papers read at our meetings; and our excellent editor, Mr. Watts, made a vigorous and successful effort, towards the close of the year, to bring the work of abstracting up to date. This has involved the printing of an extra number of our *Journal*, which is on the point of being in the hands of our Fellows.

As the duties connected with the abstraction of papers are increasingly laborious, the Society has determined to appoint a Sub-editor with special functions, and they have been fortunate in securing for this purpose the services of Mr. C. E. Groves.

A twelvemonth ago the Research Fund, which had been started by the munificence of Dr. Longstaff, and had been augmented by large donations from some of the City Companies, amounted to £3,333 13*s*. It has now reached the sum of £4,320 12*s*. It has been thought better to award in the form of grants only the interest of this money; but several grants have thus been made, and there have already been communicated to the Society two papers resulting from the assistance we have thus been enabled to render. The first by Dr. Wright and Mr. Luff, "On Some Points in Chemical Dynamics;" the second by Mr. G. S. Johnson, "On Certain Poly-Iodides." The Society's Research Fund is considered to be a matter of so much interest, and will probably be so beneficial in the future, that it has been thought

advisable to publish a separate report. It is hoped that the circulation of it will induce many other chemists, especially those to whom the pursuit of our science has become a source of wealth, to contribute handsomely to the fund.

Mr. Abel's address last year alludes to a scheme for the formation of an independent Institute of Professional Chemists. This has since been incorporated (2nd October) under the title of the "Institute of Chemistry of Great Britain and Ireland," with the two following objects:—*a*. To promote and encourage a thorough study of chemistry, and all branches of science allied thereto, in their application to the arts, to agriculture, to public health, and to technical industry. *b*. To adopt such measures as may be necessary for the advancement of the profession of chemistry, and particularly for the maintenance of the profession of the consulting and analytical chemist, on a sound and satisfactory basis. It will thus be seen that its scope is totally different from ours. We deal with chemistry in all its branches as a science; the Institute takes cognizance only of its practical applications. We are not interested in chemistry as a profession, while the Institute seeks to improve the status of practising chemists. It will thus be seen that the two societies are perfectly distinct, but may be mutually helpful. We therefore wish all prosperity to the new Institute. It held its first general meeting in our rooms, on February the 1st, under the presidency of Professor Frankland; many of the leading members of our Society have a place among its Officers and Council; while, as may be expected, a large number of chemists seek the advantages that may be derived from connection with it, as well as from our Fellowship.

The Treasurer's report will show that the financial position of the Society is not unsatisfactory, especially considering that the number of Fellows who have been elected during the past twelve months has been below the average. The funds have had an important addition from the legacy of the late C. Lambert, amounting to the sum of £1,000, in consequence of which the Council have been enabled to increase the investments by £1,500.

The number of Papers read before our Society during the past year has amounted to 65, besides two Lectures by gentlemen who have paid special attention to the subjects of general interest upon which they discoursed.

The titles of the Papers were as follows:—

I. "On the Estimation of Manganese in Spiegeleisen, and of Manganese and Iron in Manganiferous Iron Ores:" by E. Riley.

II. "On a Method of Detecting small quantities of Bismuth:" by M. M. P. Muir.

III. "On certain Bismuth Compounds. Part V:" by M. M. P. Muir.

IV. "Notes on Madder Colouring Matters, Munjistin, Purpurin, and Purpuroxanthic Acid:" by E. Schunck and H. Roemer.

V. "On some points in Gas Analysis:" by J. W. Thomas.

VI. "Experiments on the Decomposition of Nitric Oxide by Pyrogallate of Potash:" by W. J. Russell and W. Lapraik.

VII. "Contributions to the History of the Naphthalene Series. No. I. Nitroso-β-Naphthol:" by J. Stenhouse and C. E. Groves.

VIII. "On Asbestos Cardboard and its uses in the Laboratory:" by W. N. Hartley.

IX. "On a Slight Modification of Hofmann's Vapour-Density Apparatus:" by M. M. P. Muir and S. Suguira.

X. "Note on the Fluid contained in a Cavity in Fluor Spar:" by J. W. Mallet.

XI. "Examination of Substances by the Time Method:" by J. B. Hannay.

XII. "On the Dehydration of Hydrates by the Time Method. Part I. Iron and Aluminium Hydrates:" by W. Ramsay.

XIII. "On the Transformation of Aurin into Rosaniline:" by R. S. Dale and C. Schorlemmer.

XIV. "On certain Bismuth Compounds. Part VI:" by M. M. P. Muir.

XV. "On the Theory of the Luminous and Non-luminous Flames:" by J. Philipson.

XVI. "On the Gases enclosed in Lignite, Coal, and Mineral Resins from Bovey Heathfield:" by J. W. Thomas.

XVII. "On Apparatus for Gas Analysis:" by Dr. Frankland.

XVIII. "On Narcotine, Cotarnine, and Hydrocotarnine. Part V:" by C. R. A. Wright.

XIX. "On Otto of Limes:" by C. H. Piesse and Dr. Wright.

XX. "On Primary Normal Heptyl Alcohol and some of its Derivatives:" by C. F. Cross.

XXI. "On the Transformation of Aurin into Rosaniline:" by R. S. Dale and C. Schorlemmer.

XXII. "On Diamyl:" by H. Grimshaw.

XXIII. "On the Action at a High Temperature of certain Volatile Metallic Chlorides on certain Hydrocarbons:" by Watson Smith.

XXIV. "On Thallious Platinocyanide:" by R. J. Friswell and A. J. Greenaway.

XXV. "On Crystallised Barium Silicate:" by E. W. Prévost.

XXVI. "Note on Anethol and its Homologues:" by W. H. Perkin.

XXVII. "Note on Persulphocyanic Acid:" by R. W. Atkinson.

XXVIII. "On the Oxidation-Products of Aloïns:" by W. A. Tilden.

XXIX. "On some Hydrocarbons obtained from the Homologues of Cinnamic Acid, and on Anethol and its Homologues:" by W. H. Perkin.

XXX. "On two new Methods for estimating Bismuth Volumetrically:" by M. M. P. Muir.

XXXI. "On the Oxidation of Ditolyl:" by T. Carnelley.

XXXII. "Note on a New Manganese Reaction:" by J. B. Hannay.

XXXIII. "On some points in Chemical Dynamics:" by C. R. A. Wright and A. P. Luff.

XXXIV. "On the Chemistry of Cocoa Butter, Part I. Two new Fatty Acids:" by C. T. Kingzett.

XXXV. "On the Influence exerted by Time and Mass in certain Reactions in which Insoluble Salts are produced:" by M. M. P. Muir.

XXXVI. "On Nitrification:" by R. Warington.

XXXVII. "On Potable Waters:" by E. J. Mills.

XXXVIII. "On some Derivatives of Allyl-acetone:" by J. R. Crow.

XXXIX. "On a Fourth Method for estimating Bismuth Volumetrically:" by M. M. P. Muir.

XL. "On the Gas of the Grotta del Cane:" by T. Graham Young.

XLI. "Note on Tetrabromide of Tin:" by T. Carnelley and L. T. O'Shea.

XLII. "On the Bromo-derivatives of Camphor:" by H. E. Armstrong and Mr. Matthews.

XLIII. "On the Action of Iodine on Camphor:" by H. E. Armstrong and Mr. Easkell.

XLIV. "On the Constitution of Terpenes and Camphor:" by Dr. Armstrong.

XLV. "On the Hydrocarbons obtained from *Pinus Sylvestris*, with Remarks on the Constitution of the Terpenes:" by W. A. Tilden.

XLVI. "On Citric Acid as a Constituent of Unripe Mulberry Juice:" by C. R. A. Wright and G. Patterson.

XLVII. "On Cuprous Chloride and the Absorption of Carbonic Oxide and Hydrochloric Acid Gas:" by J. W. Thomas.

XLVIII. "On the Luminosity of Benzol when burnt with Non-luminous Combustible Gases:" by E. Frankland and L. T. Thorne.

XLIX. "On the Action of Reducing Agents on Potassium Permanganate:" by F. Jones.

L. "On the Action of Sulphuric Acid on Copper:" by Spencer Pickering.

LI. "On the Analysis of Sugar:" by G. Jones.

LII. "On the Decomposition-products of Quinine:" by W. Ramsay.

LIII. "On the Alkaloïds of the Aconites, Part II. On the Alkaloïds contained in *Aconitum Ferox*:" by C. R. A. Wright and A. P. Luff.

LIV. "Notes on the Tannins:" by B. H. Paul and C. T. Kingzett.

LV. "Notes on the Estimation of Phosphorus in Iron and Steel:" by E. Riley.

LVI. "An Inquiry into the Action of the Copper-Zinc Couple on Alkaline Oxy-Salts:" by J. H. Gladstone and A. Tribe.

LVII. "On a new Method for the Determination of Boiling Points:" by W. Jones.

LVIII. "On some new Derivatives of Anisoïl:" by W. H. Perkin.

LIX. "Note on the Action of Ammonia on Anthrapurpurin:" by W. H. Perkin.

LX. "On certain Polyiodides:" by G. S. Johnson.

LXI. "On an improved Form of Wash-bottle:" by T. Bayley.

LXII. "On the Preparation of Glycollic Acid:" by R. T. Plumpton.

LXIII. "On Nitrosamines:" by Otto N. Witt.

LXIV. "On a new Process for the Estimation of Cyanides:" by J. B. Hannay.

LXV. "On certain Bismuth-compounds," Part VII: by M. M. P. Muir.

Lectures.

"On the Discrimination of Crystals by their Optical Character:" by Prof. N. S. Maskelyne, F.R.S.

"On Laboratory Experiences on board the 'Challenger':" by J. Y. Buchanan, F.R.S.E.

Several of these communications have been illustrated experimentally before our audience, a course of proceeding which always adds much to the interest and profit of the evening. The Preparation-room which now exists affords the authors of papers a better opportunity of doing this than was previously the case.

The statistics of membership of the Society are as follows:—

Number of Fellows last anniversary		916
Since elected and paid admission fees		49
		965
Removed on account of arrears	13	
Withdrawn	5	
Deceased	9	
		27
Present number of Fellows		938
Number of Foreign Members last anniversary		36
Deceased		1
Present number of Foreign Members..		35
Associate elected since last anniversary.....		1

The loss sustained by the death of Fellows has not been heavy, but it includes one eminent foreign member, M. Regnault; as well as Messrs. Richard Apjohn, J. P. Gassiot, J. J. Griffin, William Gossage, Thomas Hall, E. L. Koch, Martin Murphy, Dr. H. M. Noad, and Mr. E. F. Teschemacher.

Mr. Richard Apjohn, M.A., was the son of Professor Apjohn, of Dublin, and from his boyhood evinced a great interest in those branches of science to which his father is devoted. He was educated first at the Royal School, Enniskillen, but entered Trinity College, Dublin, in 1866, and during his first year took the highest honours in mathematics. In 1870 he graduated as first Gold Medallist. In 1871 he continued his studies in Germany, in the laboratories of Professors Kekulé and Clausius. In December, 1872, he was chosen Prælector of Chemistry in Caius College, Cambridge. In 1876 that university conferred on him the degree of M.A., *honoris causa*, his lectures having been previously recognised. He also held the post of Public Analyst for Cambridgeshire, Huntingdonshire, and the Isle of Ely. He died in London, on September 12th, 1877, in the 30th year of his age, his death being the result of a fall from a bicycle. His best-known papers relate to the occurrence of vanadium and titanium in the trap-rocks of different countries, and to the analysis of a meteoric stone, and the detection of vanadium in it. The latter paper is published in our *Journal* for February, 1874. His death was heard of with much regret, as that of a young chemist of unusual promise.

Mr. John Peter Gassiot, D.C.L., LL.D., F.R.S., was born on the 2nd April, 1797, and devoted himself to scientific pursuits, while an active member of the firm of Martinez, Gassiot, and Co., of London and Oporto. His friendship with Faraday, and his connection with an electrical society formed about 1838, drew his attention especially to

electric phenomena, and he spared no expense in obtaining the best apparatus that would serve to solve the problems which suggested themselves to his mind. His spare evenings were almost always spent in the laboratory which he had fitted up in his private residence on Clapham Common, in which also he took great pleasure in exhibiting beautiful experiments to the scientific reunions for which his house was famous. He helped the cause of science also by his generous patronage, and the interest he took in the pursuits of others; and I am glad of the opportunity of acknowledging the encouragement I, for one, received from him when I was just commencing my professional career. He was one of the original founders of our Society; he took a very active part in the management of the affairs of the Royal Society, and of the British Association for the Advancement of Science. He was the originator of the Royal Society Scientific Relief Fund, and Chairman of the Committee of the Kew Observatory, which he eventually munificently endowed. For many years past he had been a magistrate of the county of Surrey; and in the city of London he was one of the leading advocates of progress in most of the social and political movements of the day. Latterly, he had been obliged to relinquish all active duties on account of failing health, and he retired to the Isle of Wight, where he died on the 15th of August, 1877, in the 81st year of his age. His scientific researches do not properly belong to the science of chemistry, except so far as voltaic electricity pertains to our province. In the years 1840 and 1844 he published in the Philosophical Transactions some experiments made with the view of obtaining a spark before the circuit of the voltaic battery was completed; and others which removed the anomaly that had puzzled previous experimenters, who found that the static effects of a battery did not increase with its chemical action. By experimenting with a Grove's battery of 100 glass cells, and paying particular attention to their insulation, he showed that the spark, the repulsion of an electroscope, the power of charging a Leyden phial, &c., did actually increase, and he thus disposed of the strongest objections to the chemical theory of the pile. Among the various points he examined was the decomposition of water under pressure, and he showed that even up to a pressure of probably 447 atmospheres, water is electrolysed, and conducts without apparently offering any extra resistance to the current. He subsequently investigated the beautiful phenomena of the stratification of the electric discharge through highly attenuated gases, first observed by his friend, Mr. (now Justice) Grove; and showed, amongst other things, that the striæ did not depend on the intermittence of the discharge, but accompanied all electric discharges in the so-called vacuum tubes; and that when the attenuation was pushed to a high degree of rarity, no electricity would pass at all.

These researches formed the subject of the Baberian lecture of 1858. Among the last of his investigations were those with powerful spectroscopes, with which he solved certain physical problems.

Mr. John Joseph Griffin was born in London in 1802, and was originally brought up to the trade of a bookseller in the firm of Messrs. Tegg and Co. He commenced business with his eldest brother in Glasgow as a bookseller and publisher, and a dealer in chemical apparatus. The publishing business was separated from the philosophical department in 1852, the one continuing under the care of his nephew, as Charles Griffin and Co., while he established the well-known firm of J. J. Griffin and Sons. He received his chemical training at Paris and at Heidelberg; and in early days he published a translation of Heinrich Rose's "Handbuch der Analytischen Chemie." He also partially edited the "Encyclopedia Metropolitana," of which his firm were the publishers. He was one of the original promoters of our Society, and was earnest in his endeavours to introduce scientific method into commercial processes, and to popularise the study of chemistry, with which latter object he wrote "Chemical Recreations," a book which has had a successful career. He was also the author of "A Treatise on the Blowpipe," "A System of Crystallography," "The Radical Theory in Chemistry," "Centigrade Testing as applied to the Arts," "The Chemical Testing of Wines and Spirits," and other papers. He took much interest in simplifying and improving the apparatus in common use. He died at Park Road, Haverstock Hill, on the 9th June last, in the 76th year of his age.

Mr. William Gossage, J.P., was born in the year 1799, and was the youngest of a family of thirteen children. His early education could not have been extensive, as he left school at the age of 12 years. He was subsequently apprenticed to an uncle at Chesterfield, who was a chemist and druggist. While there, he not only made himself acquainted with the principal chemical books of that day, but also, with the assistance of a French refugee, acquired a competent knowledge of the French language. The ardour of the teacher was not, however, equal to that of his pupil; and as he sometimes failed to be up at four o'clock in the morning for the purpose of giving his lesson, an alarum was invented for him by Mr. Gossage, which was afterwards patented.

On leaving Chesterfield, Mr. Gossage commenced business as a druggist at Leamington, and entered upon the manufacture of Leamington salts. While there he married.

In 1830 he was appointed chemist to the Stoke Prior Salt and

Alkali Works in Worcestershire. In those days open furnaces were employed, and no attempt was made to condense the hydrochloric acid. Alkali works thus became a great nuisance as the trade extended; and the attention of practical men was directed to the abating of this nuisance and the saving of the acid. These objects were attained by Mr. Gossage through the invention of his condensing towers, which were perfectly successful, and are now employed by every manufacturer of salt cake in the kingdom. Similar towers were also used afterwards for the oxidation of red liquors.

Mr. Gossage was also the first to appreciate the waste of manganese that occurred in the old process for the production of chlorine in making bleaching powder, and one of the patents he took out evidently foreshadows that with which Mr. Weldon's name is associated.

In 1841 Mr. Gossage removed to Birmingham, where he was occupied in the manufacture of white lead. In 1844 he commenced copper smelting in South Wales, and devoted much attention to the recovery of sulphur from the waste gases given off in calcining the ore. In 1848 he returned to Stoke Prior, and two years later moved to Widnes, where he established himself as an alkali manufacturer, and erected mills for crushing the limestone used in working Le Blanc's process. He also established smelting works for extracting copper and silver from the burnt Irish pyrites, which had hitherto been thrown away by the sulphuric acid makers as waste. It was here that in 1853 he first applied his condensing towers to the oxidation of black-ash liquors; and in the same year he patented a process for obtaining caustic soda directly from them, which is now in general use.

Tallow being very dear in 1854, in consequence of the Russian War, Mr. Gossage turned his attention to the manufacture of soap. After experiencing many difficulties, he succeeded in producing excellent and cheap soaps from palm oil, silicate of soda, and other materials. He subsequently commenced the manufacture of other descriptions of soap, and the works were gradually extended until they became the largest in England.

In 1857 Mr. Gossage read a paper on the history of the alkali manufacture before the British Association at Manchester; and a supplementary one in 1870 at Liverpool. He was elected a Fellow of this Society in 1862; and in 1866 was placed on the Commission of the Peace for the County Palatine of Lancaster. As an employer, he was just and considerate; as a manufacturer, honourable and energetic; and as a friend, genial and sincere.

Thomas Hall was born in London in September, 1818. His parents came from Berwick-upon-Tweed, from which town the family

removed, in consequence of his father obtaining an appointment under the Admiralty at Somerset House. Educated chiefly at University College, Mr. Hall was remarkable when very young for his love of imparting knowledge to others, and when a boy of 17 years of age he had already given several courses of instruction to working men at the London Mechanics' Institution, Chancery Lane, in recognition of which services he was made a Honorary Member, and the "Thanks of the Committee" were voted to him by a resolution dated 23rd November, 1835. Soon afterwards he proceeded to qualify for the legal profession, matriculated, and took his degree of Bachelor of Arts in the University of London.

The intention of following the law was, however, put aside by his seeing an advertisement referring to a vacancy in the then newly-established City of London School; he applied for the post, and was elected Assistant Classical and Mathematical Master in the year 1837.

When the Royal College of Chemistry opened, Mr. Hall entered as one of Dr. Hofmann's first pupils, and after a short course of study there, and at the evening classes of Dr. John Ryan at the Royal Polytechnic Institution, he, in turn, succeeded in inducing the Rev. Dr. Mortimer, late Head Master, and the Committee of the City of London School, to form a class for scientific instruction under his auspices, and, by way of experiment, a course of lectures "On Heat and the General Properties of Matter," was given in Easter Term, 1847. These lectures proved so attractive that they paved the way for the introduction of chemical studies as part of the curriculum of the school, and for twenty-one years Mr. Hall laboured so hard at his favourite theme, that the City School, with its 650 boys, became in some sort a feeder to the Institution in Oxford Street, and a regular succession of pupils was thereby induced to enter the scientific profession and proceed for further study to the Royal College of Chemistry. Amongst those who are indebted to Mr. Hall for their earliest training in science, are some of the Officers of this Society, and a score or more of its Fellows.

During the London vacations Mr. Hall occasionally visited the schools and laboratories of the Continent, for the purpose of gaining information as to the system of education pursued; and his thorough knowledge of the French language enabled him to adapt the system of his friend Dr. Ahn to English wants, and to publish, in conjunction with his brother, Mr. John Paxton Hall, the well-known little work entitled "Hall's First French Course," which was followed by a "Second French Course" for the use of more advanced students. Later on, when illness compelled his retirement from the City of London School (in the year 1868), Mr. Hall spent his winters abroad, and seemed ever ready to improve his knowledge of foreign

languages, in the acquisition of which he found great pleasure. On his leaving the City School, testimonials were presented to him both by his scientific pupils and by graduates of the Universities who had formerly benefited by his instruction. The Court of Common Council awarded him a pension, which he only lived to enjoy for about eight years, by which time the malady from which he suffered (Bright's disease) had so undermined his constitution, that he was brought home with difficulty from Switzerland, and died on the 10th July, 1877, at his son's house in Ryde, Isle of Wight, in the 59th year of his age. A few days later his remains were interred at Abney Park Cemetery in the presence of several friends and former pupils.

Mr. Hall was twice married, and leaves two children by each marriage, besides the widow, to mourn his loss. He will be remembered for his genial disposition, and for the hearty devotion and enthusiasm which characterised his work, giving encouragement to his pupils, and inaugurating within the city of London the most complete system of scientific training that had hitherto been introduced into a school course. It remains only to be mentioned that Mr. Hall spent some time in devising and perfecting a ship's pyrometer, which was intended to be used for indicating any sudden rise of temperature in the hold of a vessel loaded with coal or other inflammable cargo.

Mr. Michael Murphy, who died on the 23rd April last at the age of 48 years, was born at Ennis, in Ireland, and was intended by his parents to enter the priesthood; but their purpose being frustrated, he determined, when only 16, to go to England and carve out his own fortune. He walked in three days from Limerick to Dublin, and then on to Kingstown to catch the steamer for Liverpool. Not meeting with any employment there, he went to Newton, and accepted an engagement at Muspratt's Chemical Works. When the College of Chemistry was started at Liverpool, he was removed thence and placed in the laboratory: and he continued his connection with this Institution till, after the death of Dr. Muspratt in 1871, almost the entire responsibility of its management rested upon him from 1855 onwards. In 1854–55, Muspratt's "Dictionary of Chemistry as applied to the Arts and Sciences," was issued, the bulk of the editorial work devolving upon Mr. Murphy, who devoted 16 hours a day to it during the two years it was passing through the press. From 1864 to 1866, he was Honorary Secretary to the Liverpool Chemists' Association. He was about to enter upon the manufacture of oxide of cobalt for the supply of the potteries, and had just completed the erection of extensive chemical works at the Old Swan, Liverpool, when he was overtaken by death in 1877, leaving a widow and two daughters to mourn his loss.

Henry Minchin Noad, Ph.D., F.R.S., was born June 22nd, 1815, at Shawford, near Frome, Somerset. He was the second son of Mr. Humphrey Minchin Noad, a wealthy cloth manufacturer, and his mother was half-sister to George Canning. He was educated at the Grammar School of Frome, with the intention of entering the Civil Service of India. After the death of his distinguished relative, the hopes of a good appointment rested mainly on the friendship of Mr. Huskisson, but these were frustrated by the fatal accident to that statesman at the opening of the Liverpool and Manchester railway.

At school he listened to a course of scientific lectures, which appears to have laid the foundation of his taste for such pursuits. After leaving school he fitted up a laboratory in his father's factory, where he worked at chemistry and electricity with lightning conductors and water-batteries. When only 19 years of age, his knowledge of science and his command of language became known, and he was invited to lecture first at Frome, and subsequently at Bath and Bristol. He received encouragement in his experiments from Dr. Wilkinson of Bath, Mr. Andrew Cross, and many others. While assisting his father in his business, he found time to experiment and to publish some of his results, as well as his book on electricity. In 1839 he married his cousin, and in 1845, at the death of his father, he was left free to follow as a profession those pursuits which had been his recreation and delight from his boyhood. At once he came to London, and studied under Hofmann in the newly founded Royal College of Chemistry. In 1848 he was appointed to the Chair of Chemistry in the Medical School of St. George's Hospital, which he held till the time of his death. Soon after he obtained this lectureship, he visited Germany, and obtained his doctorate at the University of Giessen. He was elected a Fellow of the Royal Society in 1856. He was also connected with the British Association.

Dr. Noad was well known both as an author and as an investigator. In 1839 he published his "Lectures on Electricity," which soon became a recognised text-book, passing through four editions, and in 1857 giving place to a "Manual of Electricity," in two volumes; this became a standard book on all that related to the science of electricity and magnetism, and the electric telegraph of twenty years ago. He also produced a "Student's Text-book of Electricity," and in 1872 revised the new edition of Sir Snow Harris' "Rudimentary Magnetism." In 1848 he wrote a valuable treatise for the Library of Useful Knowledge, entitled "Chemical Manipulation and Analysis, Qualitative and Quantitative;" while quite recently he re-wrote Normandy's "Commercial Handbook of Chemical Analysis," a volume intended to meet the wants of the analyst, while discharging

his duties under the Adulteration Act. During the few years preceding his arrival in London, we find him examining the peculiar voltaic conditions of iron and bismuth, describing some properties of the water-battery, and elucidating that curious phenomenon the "passive" state of iron. While with Hofmann in London, his activity was directed into channels more peculiarly his master's, and we find him studying the products of the oxidation of cymene. The results were in part communicated to the Chemical Society at the time, and partly more fully elaborated and published in the "Philosophical Transactions" in later years. Among other organic products, legumin and vitellin also formed materials for his investigation about this time; but after a while he relinquished organic chemistry to occupy himself in another field. In 1850–51, he conducted, conjointly with the late Mr. Henry Gray, an inquiry into the composition and functions of the spleen. The essay resulting from this investigation gained the "Astley-Cooper" prize of 1852. We next find him devoting himself to the chemistry of iron manufacture, and in 1860 he contributed the article "Iron" to Hunt's edition of Ure's Dictionary. The experience gained during many years' study of this branch of applied chemistry increased his sphere of usefulness, and led to his being appointed consulting chemist to the Ebbw Vale Iron Company, the Cwm Celyn and Blaina, the Aberdare and Plymouth, and several other ironworks in South Wales.

In 1866 he was appointed Examiner of Malt Liquors to the India Office, and in 1872 an Examiner in Chemistry and Physics at the Royal Military Academy, Woolwich, both of which appointments he held until his death. At the time of his fatal illness he was engaged in an elaborate series of experiments in connection with the brewing of malt liquors.

Dr. Noad took little part in public proceedings, but the uprightness and worth of his personal character were highly esteemed by those friends who had the advantage of his private acquaintance.

Edward Frederick Teschemacher, the son of the well-known analyst of that name, was born at Highbury on January 23rd, 1843. His ancestors were distinguished for their eminence in science. His mother's father was Richard Phillips, one of the founders of our Society, and its President in 1849 and 1850. Her uncle was William Phillips, the associate of Conybeare in geological studies; and his own uncle James Teschemacher was the fellow labourer with Dana in the United States of America.

The subject of the present memoir began his chemical studies under Dr. Hofmann at the Royal College of Chemistry in 1859, and continued them under Professor Williamson at the laboratory of Uni-

versity College, where he took the Gold Medal for Chemistry in 1861. He then entered his father's laboratory to acquire a special technical knowledge of his profession, and remained there (his father dying in 1862) until he was taken into partnership by Mr. J. Denham Smith, the surviving member of the firm, in 1867.

He was a rapid and accurate analyst, and his published papers deal principally with practical analysis. That on the Estimation of Potash by the Chloride of Platinum method was published in 1867; that on the Estimation of Sulphur by Barium in 1871; and one on the Determination of the Amount of Morphia in Opium appeared in 1877, only a few months before his death, which took place on the 13th September.

He became a fellow of our Society in 1864, and subsequently of the Geological and Royal Geographical Societies. He was married in 1873, and has left a family of three children.

Henry Victor Regnault was born atAix-la-Chapelle, July 21, 1810. He lost both his parents when he was only eight years old, and his youth was spent in a hard battle against poverty in the effort to maintain not only himself but his sister. While still a lad, he wandered to Paris, and there obtained a situation as assistant in the large drapery establishment known as Le Grand Condé. Here ability and fidelity won for him friends, and at the age of 20 he was enabled to gratify his longing for a scientific education, and enter the Ecole Polytechnique. After a course of two years there, in 1832, he joined the Ecole des Mines, and spent three years in his studies, including visits to Belgium, Germany, and Switzerland. In 1835 he entered Berthier's laboratory, and in 1838 was made Joint Professor of Assaying at Lyons. Here he entered upon the field of research in organic chemistry which had just sprung into existence as a branch of chemical science, under the hands of Liebig, Wöhler, Laurent, Dumas, and others. While many of the chemists of the day were engaged in theoretical disputes, and the battle between the electrochemical theory and the newly advocated type theory was being hotly waged, Regnault devoted himself to the accumulation of the facts needed by the disputants on both sides. Among his investigations at this time may be mentioned those on the composition of meconine, piperine, cantharidine, and other alkaloïds; the composition of pectic acid; the identity of equisetic with maleic acid; the properties of naphthalene-sulphonic acid, &c. By the action of sulphuric anhydride on ethylene, he obtained the carbyl sulphate, $C_2H_4S_2O_6$, which Magnus prepared subsequently from alcohol. His most valuable researches, however, were on the halogen derivatives in the ethyl-group, especially interesting at the time of their appearance, when the theories of sub-

stitution were being timidly advocated. Among these compounds, now familiar reagents, were monochlorethylene chloride, $CH_2Cl.CHCl_2$, obtained by the action of chlorine on ethylene chloride, as well as the higher chlorinated derivatives, which offered one of the most striking instances of substitution. These were followed shortly after (1838) by the classical investigations on the action of chlorine on ethyl chloride, C_2H_5Cl, in which one by one all the hydrogen atoms were successively replaced by chlorine, until the limit C_2Cl_6 was reached. Regnault showed that the isomeric substitution-products obtained from chloride of ethyl and from Dutch liquid, possessed very different properties, a fact which proved that the substitution effected did not destroy the molecular grouping of the original substances. He also established the change of ether, $C_4H_{10}O$, into perchlorinated ether, $C_4Cl_{10}O$.

Another interesting series of preparations gave the substituted ethylenes by the action of alkalis on saturated halogen derivatives, ethylene bromide, for example, yielding vinyl bromide and hydrobromic acid. By this method Regnault discovered vinyl bromide, iodide, and chloride, dichlorethylene, and trichlorethylene. Finally must be mentioned his discovery of carbon tetrachloride, by passing chlorine into boiling chloroform.

It is difficult for us at the present day to estimate the importance of these discoveries forty years ago; and few series of researches have stood the test of time so well as those carried out by Regnault in his Lyons laboratory. The eighteen papers in the *Annales de Chimie et de Physique*, which contained the result of his researches, attracted the attention of the scientific world to the hitherto unknown provincial professor. In 1840 he was elected to the Chemical Section of the French Academy, and was appointed professor in the Ecole Polytechnique. In the following year he was elected to the chair of physics at the Collége de France. In 1847 he became Ingenieur en Chef des Mines, and a few years later received the order of Officer of the Legion of Honour.

With his removal to Paris, the field of Regnault's investigations was changed. Like our own Faraday, after having obtained renown as a chemist, he suddenly turned physicist. He was scarcely established there, when he began his famous series of experiments on Specific Heat. A few years previously Dulong and Petit had determined the specific heat of a number of elements by means of their calorimeter, based on their method of cooling, and obtained data sufficiently accurate to warrant the establishment of their law that the product of the specific heat of an element and its atomic weight is a constant. Regnault, after having submitted their method to careful examination, found it useless for the exact determination of the specific

heat of solids, and invented in its place the calorimeter bearing his name. It is based on the method of mixtures, viz., of heating a known weight of a substance to a known temperature, immersing it in a known weight of water at a known temperature, and determining the temperature of the mixture. With this apparatus Regnault determined the specific heat of the liquid and solid elements, and of a great variety of compounds. From the comparison of these results he deduced the general law that for all compounds of the same formula and similar chemical constitution the product of the specific heat and the atomic weight is the same. He also confirmed the hypothesis that the elements require the same amount of heat in order to be raised to a certain temperature, whether free or in combination, and showed, by his more exact results, the general truth of Dulong and Petit's law. In order to overcome the difficulties of determining the specific heat of gases, Regnault employed an ingenious apparatus in which the gases passed through a spiral inclosed in a known weight of water. The volume of gas, its temperature on entering and leaving the apparatus, and the alteration in the temperature of the water, supplied the necessary data. By this means he experimented with about thirty-five of the principal gases and vapours, and established the two important laws, 1, that the specific heat of any gas at constant pressure, whether simple or compound, is the same at all pressures and temperatures; and, 2, that the specific heats of different simple gases are in the inverse ratio of their relative densities. Regnault prepared also an interesting table of the specific heats of various substances in the solid, liquid, and gaseous forms, from which it appears that the specific heat of a body is commonly greater in the liquid than in the solid state, and always greater than in the gaseous state.

In his experiments upon heat, Regnault was led to devise methods of measuring high temperatures accurately, and invented the well-known air thermometer, which can be used at all temperatures below that at which glass softens, and the mercury and hydrogen pyrometers. He carried out also an elaborate series of experiments on the density and absolute expansion of mercury from 1° to 360°, the results of which are of primary importance in the correction of thermometers and barometers, as well as in a multitude of physical experiments. Still more elaborate and exhaustive are the series of determinations in connection with water, its specific heat at various temperatures, the tension of its vapour at various temperatures, and the latent heat of its vapour at various pressures, all intended for practical application in the construction of steam engines. For the determination of the tension of steam, Regnault contrived a simple apparatus based on the fact that the maximum tension of steam at the boiling point is equal to the external pressure, by the aid of which he was able to con-

struct his table of tensions from 0·32 mill. at 32° to 20,926 mill. at 230°.

The experiments with this apparatus were extended to a number of volatile liquids, with the design of testing the truth of Dalton's supposition, that the tension of the vapours of all liquids is the same at temperatures equally distant from their boiling points, and the results showed that it was only approximately correct. A variety of interesting results were also obtained from mixtures of gases and vapours, including the laws that a liquid does not give off a vapour of so high a tension in presence of a permanent gas as in a vacuum, and that while the tension of the vapours of a mixture of liquids not dissolving each other is equal to the sum of the tensions of the liquids at the same temperature, the tension arising from a mixture of mutually solvent liquids is less than the sum of the individual tensions.

Perhaps the most important of Regnault's experimental investigations was that on the coefficient of expansion for air and other gases, as well as on the compressibility of gases. Dalton, Gay-Lussac, and Rudberg had obtained numbers for the coefficients of expansion, differing widely from one another. It was reserved for Regnault to establish, by the most delicate experiments, the number ·03663 as the coefficient of expansion of air, and to show in addition that the law of Dalton and Gay-Lussac, with regard to the regularity of expansion among gases, was only approximately correct. A similar result was obtained in his investigations on the accuracy of Boyle and Mariotte's law on the compressibility of gases.

Regnault also made a variety of interesting experiments on the phenomena produced by heat, and his hypsometer and hygrometer should be mentioned on account of their simple and practical character. Some valuable investigations on the phenomena of respiration were made by him in connection with Reiset, and, together with Dumas, he carried out a research on illuminating gas.

His most valuable experimental results are collected together in vol. xxi of the *Mémoires* of the French Academy, and a continuation is to be found in vol. xxvi. Regnault published in 1847 a treatise on Chemistry, which has passed through numerous editions in France, and been translated into German, English, Dutch, and Italian. He was made a Fellow of the Royal Society in 1852, and obtained the Rumford and Copley medals of that body in 1848 and 1869 respectively.

In 1854 he was appointed director of the famous porcelain manufactory of Sèvres, and after that date much of his time was devoted to improvements in ceramic processes. During the Franco-German war he received a sad blow, in the death on the battle-field of his second son, Henri Regnault, a promising artist, and universal favourite in

Paris. He returned to his laboratory at Sèvres, after the declaration of peace, to find that his standard apparatus and papers, with the result of his last great research on the phenomena of heat accompanying the expansion of gases, derived from over 600 observations, had been destroyed. Since that time grief and increasing infirmities forced him to renounce his wonted pursuits. He died on the 19th of January, 1878, the anniversary of his son's death.

As a scientific investigator, Regnault did not possess the brilliant originality of many of his fellow-physicists. It was as a patient, thorough, conscientious observer that he won his way to the foremost rank. Possessing a wonderful ingenuity in the invention of mechanical appliances for the purposes of observation, and a perfect familiarity with the mathematical department of physics, he was enabled, by means of his unflagging enthusiasm and unbending resolution, to place the modern physicist and chemist in possession of an invaluable collection of constants, which are in daily use, not only in the laboratory of research, but for a large variety of industrial purposes.*

A vote of thanks to the President for his able address was proposed by Mr. De La Rue.

Dr. Frankland, in seconding the vote, referred to the establishment of the Institute, stating that he was at first anxious to have it founded in connection with the Chemical Society; this was found, however, to be impossible; and he was at one time afraid that a separate body might injure the interests of the Society; he was glad to say that his fears were groundless, and he had every reason to believe that the founding of the Institute would furnish the Society with many welcome Fellows.

The vote of thanks was put and carried.

The President, in returning thanks, said that he had endeavoured to do his best for the Society, and thanked the Members of the Council, the Officers, and Fellows for their constant and unremitting kindness to himself.

The Treasurer, Dr. Russell, then gave a statement as to the condition of the Research Fund.

Report of the Research Fund Committee.

The Research Fund Committee have to report that since the last annual meeting of the Society, the following ten grants have been made:—

* I am largely indebted for this biographical sketch to the funeral orations reported in the *Comptes Rendus* of the French Academy, and to the notice in *Nature* of January 31.

£50 to Dr. Wright for the investigation of certain problems in Chemical Dynamics.

£25 to Mr. G. S. Johnson, for a research on Double Salts with Potassium Tri-iodide.

£25 to Mr. E. Neison, for a research on Octyl Compounds.

£25 to Mr. W. Carleton Williams, for a research on Hydrocarbons containing the group Isopropyl twice.

£10 to Mr. George Harrow, for a research on Derivatives of Acetoacetic Acid.

A second grant of £50 to Dr. Wright, for the continuing of his researches on Chemical Dynamics.

£25 to Dr. Armstrong, for an investigation of Camphor and Allied Compounds.

£20 to Dr. Carnelley, for a research on the Hydrocarbons, Diphenyl, Ditolyl, Tolylphenyl, &c., and their Derivatives.

£10 to Mr. Phillips Bedson, for a research on Derivatives of Phenylacetic Acid, and on the Constitution of Isatin.

£5 to Mr. J. K. Crow, for a research on the Action of Zinc-ethyl on the Chloride of Vanadium.

Of the above grants the first five were made in July last, and the Committee are glad to be able to state that important and interesting results in connection with these investigations have already been obtained.

Dr. Wright published, in the January number of the Society's Journal, the first report on "Researches on some points in Chemical Dynamics."

Mr. Johnson has also communicated to the Society a paper on the Tri-iodides of Potassium, which will shortly appear in the Journal.

Mr. Neison informs the Committee that he has made satisfactory progress with his research; that he has prepared considerable quantities of pure octylic alcohol and octylene, as well as of octylic bromide and iodide, and has examined certain oxidation-compounds; and hopes to communicate his results to the Society before the end of the present session.

Mr. Carleton Williams states that his research has made progress, and that he has prepared pure di-isobutyl and amyl-butyl, and has examined their physical properties; that he has also succeeded in separating the primary and secondary alcohols from the mixture of isomeric chlorides obtained by the action of chlorine on di-isobutyl, and is now studying the action of bromine on di-isobutyl, and the products formed by the oxidation of the above alcohols.

Mr. Crow is engaged in carrying out his research in the laboratory of Professor Fresenius, at Wiesbaden.

The total sum thus expended this year amounts to £245.

The subscriptions and donations received during the year amount to £986 19*s*. Among the contributors are four City Companies, viz., the Worshipful Company of Drapers, of Mercers, of Skinners, and of Grocers, and the Committee are happy to state that the remaining part of this year's subscriptions has been principally contributed by those engaged in chemical manufactures; especially would they mention a donation of £229, and an annual subscription for five years of £37 2*s*., from the Alkali Manufacturers' Association. The above Association, although they in no way made it a condition, expressed a wish that Inorganic Chemistry should receive due consideration in making the grants from this fund.

At the conclusion of the report it was announced that Mr. De La Rue had offered the sum of £100 to be given to the Research Fund, on the condition that it was to be devoted to any one important research.

A vote of thanks to the Treasurer for his report, and to Mr. De La Rue for his handsome donation, was proposed by Dr. Odling, seconded by Mr. Neison, and carried unanimously.

The Treasurer then read his Report of the condition of the funds of the Chemical Society (see page 244).

A vote of thanks to the Treasurer for his lucid and satisfactory statements was proposed by Mr. Abel, seconded by Mr. E. Riley, and carried unanimously.

Dr. Odling then rose to move that the report of the President be received.

Mr. Neison, in seconding the motion, referred to the want of reagents in the Preparation Room, and the desirability of distributing the General Index of papers to all Fellows free of charge; he also made some remarks as to the present mode of electing and admitting Fellows.

In reply, Dr. Russell said that there had been no demand for reagents, but if such a demand did arise, there would be no difficulty in supplying them.

Dr. Armstrong said that he always made a point of communicating, if possible, with authors so as to have anything they might want ready for their use.

Mr. Crookes then proposed a vote of thanks to Mr. Watts, "our talented and conscientious editor."

Mr. Howard seconded the vote, which was carried unanimously.

Before electing the Council, &c., Dr. Odling asked the Secretary for information as to an alternative, which he ventured to designate an opposition, list which had been circulated; it was such an exact copy of the list issued by the Council that many Fellows thought that both lists had come from the same source.

University of Michigan

Dr. Armstrong replied that the persons issuing the list were unknown to him.

Mr. Riley thought that the name of the Fellow who issued the list ought to have been attached to it, to prevent mistakes.

Mr. Neison said that he had issued the list on his own responsibility, and that he much regretted if any one had been deceived by it. He thought, as he had proposed Mr. Kingzett at the last meeting, that every one would have known where the list came from; besides, an additional name on the list would have rendered the balloting paper illegal.

The election of Officers was then proceeded with, Messrs. Beale and Thomson having been appointed scrutators. The following were elected:—

President.—J. H. Gladstone, Ph.D., F.R.S.

Vice-Presidents.—F. A. Abel, C.B., F.R.S.; Sir B. C. Brodie, F.R.S.; Warren De La Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; W. Odling, M.B., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; A. W. Williamson, Ph.D., F.R.S.; T. Andrews, M.D., F.R.S.; W. Crookes, F.R.S.; F. Field, F.R.S.; N. S. Maskelyne; H. E. Roscoe, Ph.D., F.R.S.; R. Angus Smith.

Secretaries.—W. H. Perkin, F.R.S., and H. E. Armstrong, Ph.D F.R.S.

Foreign Secretary.—Hugo Müller, Ph.D., F.R.S.

Treasurer.—W. J. Russell, Ph.D., F.R.S.

The other Members of Council are.—I. Lowthian Bell, M.P., F.R.S.; M. Carteighe; A. H. Church; W. N. Hartley; C. W. Heaton; David Howard, G. Matthey; E. Riley; W. A. Tilden; R. V. Tuson; R. Warington; C. R. A. Wright, D.Sc.

The meeting then passed the Bye-laws as amended by the Council, with a few verbal alterations.

DR. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 27, 1877, TO MARCH 27, 1878. CR.

	£	s.	d.	£	s.	d.
Balance at Bank March 27th, 1877	1,218	6	3			
,, in hand of Treasurer	0	15	4			
				1,219	1	7
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 14th, 1877, to March 21st, 1878.						
5 Life Compositions	100	0	0			
50 Admission Fees	200	0	0			
9 Subscriptions for 1875	18	0	0			
33 ,, ,, 1876	66	0	0			
199 ,, ,, 1877	388	0	0			
556 ,, ,, 1878	1,048	13	0			
				1,820	13	0
Sale of Journal	263	7	7			
,, General Index	4	5	0			
				267	12	7
Subscriptions for Proceedings of Royal Society				52	0	0
From Public Analysts for use of Gas, Coal, &c.				3	10	0
Dividend on Consols (£4,000)	118	10	0			
,, Metropolitan Board of Works 3½ per cent. Stock	25	18	6			
,, London and North Western Railway Debenture Stock	31	2	6			
				175	11	0
Legacy from C. Lambert, Esq. (amount received)				1,000	0	0

Assets.	£	s.	d.	£	s.	d.
Balance at Coutts'	861	15	10			
,, in hands of Treasurer	4	3	7			
Three per cent. Consols	4,000	0	0			
London and North Western Railway Debenture Stock	788	0	0			
Metropolitan Board of Works 3½ per cent. Stock	1,500	0	0			
				4,538	8	2

Expenses on Account of Journal.	£	s.	d.	£	s.	d.
Salary of the Editor	250	0	0			
Fees to Abstractors of Papers	219	18	9			
Incidental expenses of Editor	5	0	0			
Periodicals for use of Abstractors	43	18	6			
Printing of Journal	817	6	6			
Distribution of Journal	126	0	7			
Honorarium to Editor	50	0	0			
				1,512	4	4
Expenses on Account of Library.						
Salary of Librarian	50	0	0			
,, Library Attendant	62	0	0			
Books and Periodicals	51	17	2			
Binding Books and Periodicals	13	11	2			
				177	8	4
Printing Authors' Copies				25	19	5
Royal Society's Proceedings				39	6	0
Reports of the Meetings				23	11	0
Miscellaneous Printing				39	7	0
Insurance of Society's Furniture and Books				2	0	0
Stationery, Postage, Envelopes, Receipt Books, &c.				19	1	4
Expenses connected with Lectures				11	5	2
Inhabited House and Income-tax				4	10	0
Legal Expenses				47	18	6
Collector's Commission on Subscriptions				91	0	0
Treasurer's Stamps, Draft Stamps and Clerical Aid				5	5	9
House Expenses.						
Provision of Refreshments at Meetings	24	13	1			
Heating of Building	18	7	0			
Lighting of Building	35	8	10			
Cleaning of Building	19	6	8			
Petty House Expenses	10	6	7			
Wages of House Porter	37	6	0			
Gratuity to Gate Porter	2	2	0			
Petty Cash Disbursements	0	9	3			
				147	19	5
Purchase of £1,000 Metropolitan Board of Works 3½ p. c. Stock				1,013	15	0
Purchase of £500 do. do.				511	17	6
Balance at Coutts'	861	15	10			
,, in hands of Treasurer	4	3	7			
				865	19	5
				4,538	8	2

TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.

DR. FROM MARCH 27, 1877, TO MARCH 27, 1878. CR.

	£	s.	d.
Balance at bank March 27, 1877	275	8	7
Subscriptions and donations	986	19	0
Dividend on North British Railway Stock	39	10	0
„ Metropolitan Board of Works 3½ per cent. Stock	82	1	11
	£1,383	19	6

		£	s.	d.
1877.				
May 31.	By purchase of £500 Metropolitan Stock	508	2	6
July.	By grants made	135	0	0
1878.				
Feb.	By grants made	110	0	0
	By purchase of £400 Metropolitan Stock	411	10	0
	By balance	219	7	0
		£1,383	19	6

Assets.	£	s.	d.	
Metropolitan Board of Works 3½ per cent. Stock	2,900	0	0	
North British Railway Stock	1,000	0	0	
Balance at Bankers	219	7	0	
				£4,119 7 0

XXVII.—*A New Process for the Volumetric Estimation of Cyanides.*

By J. B. Hannay, F.R.S.E., Assistant Lecturer on Chemistry, The Owens College, Manchester.

The processes at present in use for the volumetric estimation of cyanides by solution of silver and iodine requiring, as they do, the absence of such frequently-occurring substances as ammonia and alkalis, and depending on solutions prone to change, are in so far faulty; and as besides it is often desirable to estimate the cyanide in an alkaline solution already containing silver cyanide, I have considered that the description of a process (which I have used for some years), and which is interfered with by no commonly occurring bodies, may have some interest for this Society. The process is the converse of that for the estimation of mercury, of which I published an account (*Chem. Soc. Jour.*, June, 1873, vol. xxvi, p. 565) some years ago, and which has just received such complete confirmation (*Chem. Soc. Jour.*, December, 1877, vol. ii, p. 679) at the hands of Professor Tuson and Mr. Neison; in fact, it was the publication of their paper that induced me to write the present note. The process for the estimation of cyanogen in compounds depends on the anomalous behaviour of mercuric cyanide with alkalis; so that, if to an alkaline solution containing cyanogen a mercuric salt is added, no precipitate takes place until all the cyanogen is combined with mercury; that is to say, as long as the decomposition $2KCN + HgCl_2 = Hg(CN) + 2KCl$ goes on, all the mercury existing as cyanide is not affected by alkalis. The cyanide is dissolved in water, placed in a beaker on a black slab (or black velvet), rendered alkaline preferably with ammonia, and a standard solution of mercuric chloride is added in successive quantities, with frequent stirring, until a permanent bluish-white opalescence is produced. The end of the reaction is sharply marked, and half a drop of a centinormal solution is sufficient to produce a strong opalescence.

To test the accuracy of the process, as well as to find if other substances had any interfering action, a solution of potassic cyanide, containing 0·00651 gram per c.c. (decinormal), was prepared, and the strength checked by silver estimation. A decinormal solution of mercuric chloride was also prepared, containing 0·0271 of the chloride per c.c. A portion of this solution was reduced to half strength, that is, containing 0·01355 per c.c., so that one c.c. of this was equal to one c.c. of the cyanide. It was found that 20 c.c. of the cyanide gave a

perceptible opalescence, when a small fraction over 20 c.c. of the mercury solution had been added; the excess was less than ·03 of a c.c. in an average of five estimations. To find how little would really show the turbidity, I prepared a centinormal solution, and reducing it to half strength, I found that 20 c.c. of the decinormal cyanide required 200·1 c.c. of the mercury solution to produce a decided opalescence; but that was the highest, other experiments requiring between ·05 to ·08 c.c. of excess. This indicates a quantity of ·0000651 of the cyanide, or an error of ·05 per cent. A large number of experiments were made on the action of alkaline sulphates, chlorides, and nitrates, but with the same result as Tuson and Neison have already shown. I also found that very large quantities of ammonium salts prevent the appearance of the opalescence when small quantities of cyanides have to be estimated; but as the above authors have shown that the interference begins only when 15 times more ammonium salt is present than of mercury, it will be seen that in ordinary chemical analysis such a state of affairs seldom arises. The kind of impurities in which I was more interested, however, were those present in samples of commercial potassic cyanide, principally potassic cyanate and thiocyanate, as caustic alkalis and alkaline carbonates are entirely without action. Solutions of the cyanate and thiocyanate were prepared, containing ·05 gram per c.c., and the following experiments were tried. Cyanate: 20 c.c. of the cyanide were measured off, and 10 c.c. of the cyanate solution added; and after rendering alkaline with ammonia, mercuric chloride (decinormal half strength) was added, when it was found that a single drop over 20 c.c. caused an opalescence. Two other experiments were tried, using 20 c.c. and 50 c.c. of the cyanate; the two took 20·05 and 20·08 to produce an opalescence. The fractions were done by completing the process with centinormal solution: thus it will be seen that cyanic acid has no effect on the process. Three other experiments were done, using very dilute solutions, but still there was practically no effect. Thiocyanate: as before, 20 c.c. of cyanide and 10 c.c. of thiocyanate were rendered alkaline with ammonia and the mercury solution added. It took 20·2 c.c. of the mercury. Two others with 30 c.c. and 50 c.c. of thiocyanate respectively took 20·6 and 21 c.c. of mercury solution. I suspected that the thiocyanate could not be quite pure, so I recrystallised some of what had appeared to be pure salt, and I found that it now had no effect; three quantities of 20 c.c. each, with 10·30 and 50 c.c. of thiocyanate, taking 20·01, 20·04, 20·07 for the production of the opalescence. It will thus be seen that thiocyanic acid has also no effect upon this process. As it is often desirable to estimate cyanides in a solution containing silver, as in electro-platers' baths, I added silver nitrate to three quantities of cyanide solution in the following proportions:—

I. To 20 c.c., a quantity not sufficient to cause a precipitate.
II. „ just sufficient to cause a precipitate.
III. „ a large excess.

On adding a little ammonia to I and dissolving the precipitates II and III in ammonia, each took a very small fraction over 20 c.c. of mercuric chloride solution to produce an opalescence. This shows that silver salts do not interfere with the process. It will thus be seen that we have now a process by which cyanogen in combination can be estimated accurately, even in the most complex mixtures; and as mercuric chloride can easily be obtained pure and keeps unaltered in solution, the process is one of great facility.

XXVIII.—*On Terpin and Terpinol.* (*Preliminary.*)

By William A. Tilden, D.Sc., Lond.

Terpinol is the name given by List to the liquid obtained by the action of dilute acids upon terpin hydrate, but the statements of Wiggers (*Ann. Chem. Pharm.*, 1846, i, 251), List (*ibid.*, 1848, 362), and Oppenheim (*ibid.*, 1864, 149), regarding the composition and properties of this substance are at variance with one another.

Terpinol is described by List as a liquid of specific gravity ·852, boiling constantly at 168°. On the other hand, Oppenheim states that when terpinol is distilled it begins to boil at 165°, and that the temperature gradually rises to 208°. Moreover, Oppenheim asserts that distillation causes a decomposition in terpinol in such a manner that the first portions of the distillate contain more carbon and less hydrogen and oxygen than the last. The analyses of Wiggers and List indicate the formula $C_{20}H_{34}O$ or $(C_{10}H_{16})_2OH_2$.

My experiments lead me to conclusions differing materially from those of the chemists to whom I have referred, and although the subject is by no means complete, I beg leave to bring before the Society such results as I have obtained.

Crystallised Terpin, $C_{10}H_{20}O_2.OH_2$.

This beautiful compound was prepared by a process essentially the same as that given many years ago by Wiggers. I find that it is advantageous to use a rather large proportion of nitric acid. A mixture of 1 measure of nitric acid (sp. gr. 1·4), 1 measure of methylated spirit, and $2\frac{1}{2}$ measures of rectified turpentine oil becomes very warm,

and in about two days loses the smell of turpentine. If such a mixture is then poured out into an open dish, a small quantity of methylated alcohol being added every few days, it deposits crystals which in about a fortnight amount to one-third of the weight of the turpentine employed. More crystals are obtained by prolonged exposure.

I have ascertained that no crystalline compound is formed under similar circumstances from the terpenes of the orange group; also that the same compound is obtained whether American or French turpentine oil be employed.

The crystals from both sources agree in melting point, in crystalline form, and in giving an alcoholic solution which does not act upon a ray of polarised light.

Action of Dilute Hydrochloric Acid upon Terpin.

Separate experiments were made upon the terpins obtained from the two kinds of turpentine oil. The product is, however, always the same, and it will be necessary therefore to quote only one experiment.

To 53½ grams of crystallised terpin, boiled up with 700—800 c.c. of water, 12 drops of hydrochloric acid were added. In a few minutes the crystals had disappeared, and the liquid, now turbid from the presence of oily matter, was distilled. A distillate of peculiar and fragrant odour was obtained. When about half the liquid had passed over, a little water containing 12 more drops of hydrochloric acid was added to the residue in the flask, and the distillation continued until all the oil had distilled over. I retain the name terpinol for the oily product.

When this terpinol was submitted to distillation, the temperature went up immediately to above 200°, and all but a few drops came over between 205° and 215°. When redistilled it came over again between the same limits of temperature, but no product of more definite boiling point was obtained.

It undergoes no change of properties by distillation; neither is it changed appreciably in composition. Two analyses were made, the one of the crude product dried by chloride of calcium, but not redistilled (1); the other of the liquid redistilled, and collected between 205° and 215°.

1. ·18925 gram gave ·5445 of CO_2 and ·2080 of OH_2.

2. ·2803 gram gave ·8110 of CO_2 and ·3010 of OH_2.

These results give percentages of carbon and hydrogen, which closely approximate to the numbers calculated from the formula $C_{10}H_{18}O$ or $C_{10}H_{16}.H_2O$.

	1.	2.	Calculated.
C....	78·3	78·9	77·9
H....	12·2	11·9	11·7

The formula $C_{20}H_{34}O$ or $(C_{10}H_{16})_2OH_2$ requires C 82·75, H 11·72 per cent.

Whether the formula $C_{10}H_{18}O$ correctly represents the molecular weight of this compound is a question which cannot be finally determined till the vapour-density has been taken and further experiments made. For the present I am much disposed to consider that this formula should be doubled, and that terpinol should be regarded as the anhydride or ether of terpin, bearing in fact a relation to that compound similar to the relation of common ether to ethylic alcohol.

Terpin being—

$$C_{10}H_{18}\begin{cases}OH\\OH\end{cases}$$

terpinol must be written

$$C_{10}H_{18}<\begin{matrix}O\\O\end{matrix}>C_{10}H_{18}.$$

Almost conclusive evidence of this is supplied by the action of hydrochloric acid, which does not give a monochloride, as might be expected if terpinol had the constitution expressed by $C_{10}H_{17}(OH)$.

Terpinol is a colourless, somewhat viscid liquid, inactive upon the polarised ray, and having at 16° a specific gravity ·9274. When dry hydrochloric acid gas is passed into it, the liquid becomes very hot, and assumes an intense purple colour. It ultimately sets into a mass of crystals, which after strong pressure become perfectly white. These crystals were analysed, and found to contain 33·94 per cent. of chlorine. They melt at 50°. The compound is therefore identical with the dihydrochloride, $C_{10}H_{18}\begin{cases}Cl\\Cl\end{cases}$, obtained by saturating terpin with hydrochloric acid gas; also by saturating with hydrochloric acid a solution of turpentine in ether or alcohol.

This compound is entirely converted into terpinol by boiling for an hour or two with water.

When this dichloride is boiled for a few minutes with a solution of sodium in absolute alcohol, a precipitate of common salt is thrown down; and on adding water to the liquid an oil separates, which becomes slightly yellow on exposure to air. In contact with ordinary strong hydrochloric acid, it is instantly converted into a crystalline mass of dichloride. It was found to contain 24·9 per cent. of chlorine.

The formula $C_{10}H_{18}\begin{cases}OC_2H_5\\Cl\end{cases}$ requires 16·24 per cent. of chlorine. I am therefore in doubt whether this compound was formed, or whether the liquid examined was a solution of the dichloride in the compound $C_{10}H_{18}\begin{cases}OC_2H_5\\OC_2H_5\end{cases}$.

Terpinol is miscible with alcohol in all proportions. If the alcoholic

solution is acidified with nitric acid and placed in a dish, it deposits in a few hours abundant crystals of terpin. This fact, and the peculiar odour of the liquid left in the preparation of terpin by the ordinary process, lead me to the belief that terpinol is formed at a certain stage of the reaction between turpentine oil, alcohol, and nitric acid.

$$C_{10}H_{16} + C_2H_5OH + HONO_2 = \underset{\text{Terpinol.}}{C_{10}H_{18}O} + C_2H_5ONO_2.$$

The liquid which has begun to deposit crystals, when separated, washed free from nitric acid, and heated, evolves nitric oxide and then distils chiefly between 200° and 230°. I look upon the production of terpin as probably accomplished through the intermediate formation of a compound of terpinol with the elements of ethyl nitrate,

$$C_{10}H_{18}O\left\{\begin{matrix}OC_2H_5\\NO_2\end{matrix}\right.,$$

which is subsequently decomposed by water.

$$C_{10}H_{18}O\left\{\begin{matrix}C_2H_5\\NO_2\end{matrix}\right. + 2H_2O = \underset{\text{Terpin.}}{C_{10}H_{18}\left\{\begin{matrix}OH\\OH\end{matrix}\right.} + C_2H_5OH + NO_2OH.$$

The same succession of changes may be supposed to be repeated indefinitely.

Action of Sulphuric Acid on Terpin.

76 grams of terpin crystals were placed in a large flask, together with about 50 grams of sulphuric acid diluted with seven or eight times its bulk of water. Steam was passed through the mixture, till all the oily matter had distilled over. After separating from the water the product was found to distil entirely between 177° and 187°. After redistillation a portion was collected between 176° and 177°, and analysed. It gave 84·7 per cent. of carbon and 11·8 per cent. of hydrogen. The formulæ $(C_{10}H_{16})_2OH_2$ and $C_{10}H_{16}$ require respectively 82·75 and 88·2 per cent. of carbon.

The product was therefore presumed to be a mixture of terpinol with a hydrocarbon. It was boiled for two to three hours with about two volumes of water and one volume of oil of vitriol. The product fractioned and finally distilled from sodium gave about one-third of its bulk at 176—178°, and this portion when burnt gave numbers corresponding with 87·33 per cent. of carbon and 11·8 of hydrogen in one experiment, and 87·43 per cent. of carbon and 11·79 of hydrogen in a second. Its vapour-density was taken by Hofmann's method in aniline vapour, and was found to be 68·8.

This, then, is evidently a hydrocarbon, having the formula $C_{10}H_{16}$.

	Theory.	
C	88·2	
H	11·8	Density .. 68

It seems to stand in the same relation to terpin as ethylene to common alcohol, and it is probably formed by a similar reaction. It is, however, exceedingly difficult to get rid of the last traces of terpinol which accompany it. After very careful purification, another specimen boiling at the same temperature, namely, at 176—178°, had a specific gravity of ·8526 at 15°. This compound is optically inactive. Treated with hydrochloric acid it gave no crystalline deposit, but after exposure in a dish for several days, the liquid left a few crystals of the dichloride $C_{10}H_{18}Cl_2$. These were attributed to the presence of a small quantity of terpinol in the specimen operated upon. No crystalline nitroso-compound could be obtained by the action of nitrosyl chloride. When diluted with chloroform, cooled, and mixed with two equivalents of bromine, it gave a dibromide which on heating splits up into hydrobromic acid and cymene, yielding a quantity of the latter compound equal to half the weight of the hydrocarbon operated upon.

In many respects this hydrocarbon agrees with the terpene characteristic of Russian turpentine oil, and described in a recent paper of mine (*J. Chem. Soc.*, February, 1878). It differs, however, from that compound in having no action on polarised light, and to the extent of about 4° or 5° in the observed boiling points.

The oxidation products are of course very important, and I have ascertained that both terpinol and terpinylene, as this hydrocarbon may be called, yield, besides other acids, an appreciable quantity of toluic acid melting at 176°. I do not regard this as a serious obstacle to the acceptance of the formulæ for the terpenes I have lately proposed. Assuming these hydrocarbons to consist of an open chain, which is liable to be closed by the removal of hydrogen from the terminal carbon atoms, it is not improbable that this closing of the chain may be effected during processes of oxidation. But that this occurs in a fortuitous and irregular manner is shown by the very small amount of the toluic or terephthalic acid ever obtained from any of the $C_{10}H_{16}$ group. Cymene, $C_{10}H_{14}$, in which we must admit the closed benzene ring, yields under the same circumstances something like a third of its weight.

XXIX.—*The Poisonous Principle of Urechites Suberecta.*

By James John Bowrey, Analytical Chemist to the Government of Jamaica.

The plant which has yielded the substances to be described in this paper is very common in Jamaica, occurring sometimes in clumps standing by itself, but far more commonly climbing over fences, or clinging to low growing shrubs. Its dark-green leaves and large bright yellow flowers render it very conspicuous in the hot, dry districts in which it flourishes. In the island it is called "Nightshade," in consequence of its deadly character, but Professor Daniel Oliver has kindly identified it for me as *Urechites suberecta, Muell. Arg.* (*Echites Neriandra Griseb*).

My attention was specially directed to this plant by the wonderful tales told of its poisonous powers in the hands of those acquainted with its properties, it being stated that they could so administer it as to cause the very speedy death of the victim, or so as to kill only after the lapse of weeks or months. It is believed to have been used with comparative frequency in the time of slavery, as a means of getting rid of obnoxious masters, and is supposed to be occasionally used at the present time as an instrument of crime.

The leaves are intensely bitter and very acid, producing a sensation on the lips and tongue of being swollen and blistered, though their aspect is quite unchanged. The powder of the leaves applied to the nostrils causes violent sneezing, hence it was necessary to take precautions in powdering them, or unpleasant effects followed. These active properties are possessed by all the green parts of the plant and by the flowers, but exist very slightly, if at all, in the woody portions. My researches have been confined to the leaves and green tips of the plant, from which I have obtained three substances, characterised in a high degree by their physiologically active qualities. These active bodies I have named Urechitoxin, Amorphous Urechitoxin, and Urechitin.

Preparation of Urechitoxin and Amorphous Urechitoxin.

The active principle of the plant is dissolved out by water, but the extraction is very incomplete, even when large quantities of water are used, while a great amount of inactive matter is also taken up which complicates the subsequent purification. Alcohol easily and completely removes the bitter substance, but unless it be nearly absolute, it also takes up much extractive matter; on the other hand, if very

strong, it dissolves green resinous matter, which is, however, easily got rid of by dilution. These observations led me to the following process :—The leaves and green tips were first air-dried, and then at 100° C., as long as they gave off moisture, air also heated to 100° C. being passed over them to hasten the drying. The now very crisp and brittle leaves were finely powdered as rapidly as possible, so as to avoid absorption of moisture from the atmosphere, and the powder was extracted with spirit of at least 98 per cent. alcoholic strength. If maceration was continued for a sufficiently long time, a comparatively small volume of spirit rendered the extraction practically complete. The dark-green tincture obtained was distilled to recover part of the spirit; but if it was well made, and therefore very strong, distillation was advantageously dispensed with; whether or no, the next step was to add about an equal bulk of boiling water, pouring it into the tincture gradually, and stirring vigorously meanwhile; this caused a green coloured resinous precipitate, which was removed by filtration, and after washing with spirit of 50 per cent. alcoholic strength, was found to be devoid of bitter taste.

The clear filtrate, now of a yellow-brown colour, was mixed with the washings, and a strong solution of basic acetate of lead added as long as a *yellow* precipitate fell, care being taken not to add more than just enough for this purpose, or a loss of urechitoxin resulted from its partial precipitation together with the coloured precipitate. This loss is due simply to dilution of the spirit by the lead solution. The yellow precipitate was filtered off, and washed once or twice with spirit of 50 or 60 per cent.; prolonged washing would remove all bitter matter from it, but is not economical. The mixed clear yellow filtrate and washings were next freed from lead by means of sulphuretted hydrogen and filtration, and as much urechitoxin is carried down by the lead sulphide, it must be well washed with hot spirit of 50 or 60 per cent. On evaporation in a vacuum over sulphuric acid, the acid liquors deposited small white crystals; when their quantity ceased to increase, the mother-liquor was removed by means of the filter-pump, and evaporated to dryness over oil of vitriol in a vacuum, yielding a resin-like mass of crude amorphous urechitoxin. The crystals were washed on the filter with spirit of 20 per cent., and then dissolved off in a little boiling 30 per cent. spirit. The solution was quite colourless, and on cooling microscopic crystals of urechitoxin separated out in such quantity as to render the whole mass pasty; they were collected on a Bunsen's filter, washed with a little cold 30 per cent. spirit, and dried in a vacuum. The mother-liquor and washings evaporated in a vacuum over oil of vitriol yielded a further crop of urechitoxin, and a little amorphous urechitoxin.

The crude amorphous urechitoxin mentioned above was dissolved in

a little absolute alcohol, to get rid of any inert extractive matter present, the solution evaporated at a gentle heat until syrupy, and while it was still-warm, hot water was added gradually, the mixture being vigorously stirred all the time, so as to bring the water into contact with every part of the resulting soft resin. After removing the water, the resinous mass, if nearly colourless, was heated on the water-bath for a few minutes, then placed over oil of vitriol, and a vacuum produced as quickly as possible; this caused it to swell and froth up, and speedily lose all moisture, the product being a porous, easily powdered, light amber-coloured mass of amorphous urechitoxin. If, however, the resin precipitated by the hot water was dark in colour, it was dissolved in spirit of 50 or 60 per cent., and purified animal charcoal added until most of the colour was removed, the charcoal separated by filtration, and the filtrate evaporated nearly to dryness at a gentle temperature, and finally dried in a vacuum as described above.

I found it impossible entirely to bleach solutions of amorphous urechitoxin by means of animal charcoal, and even sufficient charcoal to remove most of the colour abstracts a large proportion of the poison; it is therefore necessary to wash the charcoal with boiling spirit of about 60 per cent., in order to avoid a considerable loss of amorphous urechitoxin. Urechitoxin and urechitin are also removed, more or less, from their solutions by animal charcoal.

Much of the urechitoxin and amorphous urechitoxin I have prepared has been obtained by the foregoing method, but samples have also been made by the following modified and less troublesome process. After the removal of the lead by sulphuretted hydrogen, the liquid was distilled in a vacuum, nearly to dryness, at a temperature not exceeding 35°, whereby a soft resinous residue, perfectly homogeneous and free from crystals, was obtained; it was mixed with several times its bulk of spirit of 15 per cent., and allowed to stand for several days, when its appearance was found greatly changed; it now consisted of a mass of microscopic crystals of urechitoxin, mixed with more or less amorphous urechitoxin in the form of minute oily drops. The weak spirit was of a dark colour, being charged with the more highly-coloured portions of the residue; it was drawn off by the filter-pump, and the crystals freed from amorphous urechitoxin by washing with successive small quantities of 20 per cent. spirit, and finally with a little 30 per cent. The final operations to obtain the two forms of the poisonous principle in a pure state were the same as those already described.

From the perfectly dried leaves of the *Urechites suberecta* I have obtained as much as 1 per cent. of urechitoxin, and nearly 3 per cent. of mixed urechitoxin and amorphous urechitoxin. On an average the

fresh leaves lose four-fifths of their weight on being completely dried; they must therefore contain rather more than one-half per cent. of their active principle.

In one operation a much larger proportion of water than that recommended above was mixed with the tincture, and no care was taken to conduct the evaporation at a low temperature, or to prevent access of air, the large amount of liquid present being driven off by the heat of an ordinary water-bath. The result was an unsatisfactory yield of amorphous urechitoxin, while no crystalline product whatever was obtained.

After a satisfactory process for the preparation of urechitoxin had been worked out, the various samples obtained were mixed and recrystallised from 30 per cent. spirit, the yield being about two ounces of dry crystals: Sample A.

A small portion of A was recrystallised three times from 30 per cent. spirit, the crystals being freed from their mother-liquor each time by washing with spirit of the same strength: the result was Sample B.

Another sample, C, was prepared by slow crystallisation from a solution of a portion of Sample A in 60 per cent. spirit. When but a fraction of the amount in solution had separated the crystals were collected, washed, and dried.

Samples A and B consisted of microscopic crystals perfectly clear and transparent singly, but snow-white in mass. The crystals in C were much larger, being nearly half-an-inch long.

Preparation of Urechitin.

The fact that occasionally no urechitoxin and but little amorphous urechitoxin was obtained from the dried leaves, coupled with some observations made in the preliminary experiments of this research, led me to suspect that the poisonous principle of the plant underwent some change either in the process of drying or in the subsequent manipulations. If not, why was it that occasionally nothing but the amorphous form was obtained? The experiments now to be detailed shed some little light on this question, and led to the discovery of the form of the poison which I have called urechitin.

Five pounds of fresh leaves were finely minced and then exhausted in a displacement apparatus with successive quantities of nearly absolute alcohol, in all fifteen pounds of spirit being used. The tincture which came through first was dark brown, then followed some of a dark green, while the portions which came through as the exhaustion approached completion were light green: these were put on one side. On mixing the brown and dark green tinctures, much green matter

separated, which, after being washed with 50 per cent. spirit, was found to be free from bitter taste; it was removed by filtration, and the clear yellow-green filtrate run into a bolt-head connected with another and larger one immersed in ice. The air was next pumped out of the vessels, and the smaller one surrounded with warm water; distillation now proceeded briskly at temperatures ranging from 28° to 38°. As the alcohol passed over, crystals contaminated with a little green resinous matter separated. The distillation was continued until the liquid began to froth over into the condensing vessel; the crystals were then collected on a filter, and the mother-liquor returned to the bolt-head and distillation in a vacuum again started, frothing being prevented by gradually running in the light-green tincture which had been put on one side; this weak tincture was run in so that the vacuum was not injured, and at such a rate as just to avoid frothing. By this manipulation the distillation was carried on to dryness at a temperature not exceeding 38°. The dry residue was treated with nearly absolute alcohol in considerable quantity, whereby all bitter substance was dissolved, and much brown gummy matter left behind. The alcoholic solution was diluted with enough hot water to reduce its alcoholic strength to about 40 per cent.; this caused the precipitation of much inert green matter, which was removed by filtration, and was washed with a little hot 40 per cent. spirit. The washings and filtrate were returned to the bolt-head (from which of course the inert gummy matter had been cleaned out), and on standing deposited some white crystals, the quantity of which was greatly increased by distilling off the alcohol in a vacuum, as already described. When all the spirit had passed over, the crystals, which were now of a dirty green colour in mass, were collected on a filter and washed with water. The filtrate was of a brownish-yellow colour and very bitter; on evaporation it left a not very considerable residue giving the colour reaction of the poisons (to be described further on), but as if much foreign matter was present. It has not yet been further examined.

The crystals were dissolved in 80 per cent. spirit, and an alcoholic solution of basic acetate of lead added as long as it caused a precipitate, which was then removed by filtration and washed with strong spirit. The mixed filtrate and washings were next freed from lead by a stream of sulphuretted hydrogen and filtration, then distilled in a vacuum until most of the alcohol had passed over. A quantity of nearly colourless crystals of urechitin having separated during the distillation, they were collected and put on one side for further purification. The mother-liquor, on evaporation to dryness, yielded a comparatively small amount of what appeared to be amorphous urechitoxin containing a few crystals of urechitin.

The purification of the crystals mentioned above was effected in the

following manner; they were ground in a mortar with barely enough nearly absolute alcohol to form a thin paste, and the mixture, after standing in a closed vessel for several hours, was thrown on a Bunsen's filter, the alcoholic solution drawn through as completely as possible, and the powder washed with successive small volumes of the same alcohol as long as it came through coloured. The mixed alcoholic filtrates had a light yellow colour, and on slight dilution with water, deposited some pure white crystals, which were collected and added to the powder on the filter. On further dilution, more crystals were precipitated, but now mixed with much resinous matter (? amorphous urechitoxin), from which I did not succeed in separating them.

The mass of white powder and crystals were dissolved at a temperature of 60° in barely sufficient 70 per cent. spirit, and the clear solution allowed to cool very slowly; by next morning a fine crop of perfectly colourless crystals had formed, which were collected, washed with a little 60 per cent. spirit, dried in a vacuum over quick lime, and bottled. The bottle was labelled, "Urechitin, Sample A."

The mother-liquor was slightly coloured, a *little* animal charcoal served to decolorise it, after which it was distilled in a vacuum as long as alcohol came over; the crystals which formed as the alcohol passed off were collected (the watery mother-liquor held hardly anything in solution), dissolved in strong hot spirit; and warm water was added so as to reduce the alcoholic strength of the solution to about 40 per cent. Crystals began to form at once and increased in quantity as the solution cooled; they were filtered off and washed. Their mother-liquor, on still further dilution, deposited more crystals having the same appearance and properties as those first formed; the two crops were therefore mixed, dried over quick-lime in a vacuum, and labelled, "Urechitin, Sample B."

On further treatment, the liquors from B yielded a small amount of a bitter resin resembling amorphous urechitoxin, and also a minute quantity of a crystallisable body like urechitoxin, but the amount obtained was too little to enable me to determine if the two were really identical.

The water in the fresh leaves complicating the extraction of the urechitin, I made an experiment to ascertain whether drying at ordinary temperatures would alter the result obtained from the fresh leaves. Five pounds of leaves were allowed to dry in the air as long as they lost weight, their weight ultimately falling to 22½ ounces; an experiment on a few grains of these air-dried leaves proved that at a temperature of 100° they would lose nearly three ounces more. The 22½ ounces were reduced to a fine powder, and exhausted with nearly absolute alcohol, seven pounds of which served to remove all soluble matter. The tincture was treated much in the same manner

as that from the five pounds of fresh leaves, but no basic acetate of lead was used in this experiment; in fact, nothing but alcohol, water, and a little animal charcoal were employed to obtain the urechitin in the pure state. This operation gave me three samples of crystals, viz.:—

Urechitin, Sample C. A small sample of fine bold crystals, produced by a very partial and slow evaporation, in the cold, of a solution in 80 per cent. spirit of the total quantity of crystals obtained.

Urechitin, Sample D. Procured from the mother-liquor of Sample C by diluting it with hot water until its alcoholic strength was reduced about one half. The solution was frequently shaken as it cooled, and deposited the crystals more massive, though somewhat irregular, than any other sample I have prepared excepting C.

Urechitin, Sample E. A small sample of minute crystals separated from the mother-liquor, and washings of D, by distilling off the alcohol in a vacuum. As this sample proved by its reaction and also by the numbers it gave on combustion, to be contaminated with a small quantity of some other substance, I shall not again mention it.

These three samples weighed 167 grains, equal to a yield of 0·48 per cent. of the weight of the fresh leaves used. As the loss of urechitin in the process of purification plainly far more than equalled the weight of impurity present in Sample E, it is safe to conclude that the fresh leaves contain at least one-half per cent. of urechitin.

Urechitoxin

contains no nitrogen. The carbon and hydrogen were determined in each of the three samples after drying at 100° C., with the following results:—

		Obtained.		Percentage.	
	Taken.	CO_2.	H_2O.	C.	H.
A.	0·2370 gram	0·5314 gram	0·1682 gram	61·15	7·89
	0·2266 „	0·5088 „	0·1610 „	61·24	7·89
B.	0·2039 „	0·4580 „	0·1443 „	61·26	7·86
	0·2876 „	0·6478 „	0·2044 „	61·43	7·90
C.	0·1650 „	0·3709 „	0·1165 „	61·31	7·85

These figures prove the three samples to be practically identical, and give a mean of C 61·28, H 7·88, O 30·84, as the percentage composition of urechitoxin. The formula, $C_{13}H_{20}O_5$, is the simplest which fairly well represents these percentages:—

$$C_{13}H_{20}O_5 \text{ requires} \begin{cases} C\ 60{\cdot}94 \\ H\ 7{\cdot}81 \\ O\ 31{\cdot}25 \end{cases}. \quad \text{Analysis gives} \begin{cases} C\ 61{\cdot}28 \\ H\ 7{\cdot}88 \\ O\ 30{\cdot}84 \end{cases}.$$

From spirit of about 30 per cent. alcoholic strength urechitoxin usually crystallises in thin four-sided prisms, bounded at each end by

two planes, from very weak spirit or water in sharp pointed needles; it does not crystallise readily from strong spirit, indeed I doubt if crystals can be obtained from alcohol approaching absoluteness. The crystals break across their length very readily.

After being dried between folds of bibulous paper, urechitoxin still retains about 8 per cent. of water, which is lost over oil of vitriol or more rapidly at 100°, no further loss results from heating to 120°. If the dry crystals be exposed to the atmosphere for a few hours, they gain from 8 to 9 per cent. on their dry weight. The exact amount of gain seems to depend on the temperature, the increase of weight in the laboratory at Kingston, Jamaica, with an average temperature of 29°, being one-ninth less than that noticed in some experiments made in the South Kensington Research Laboratory, with an average temperature, during the period of exposure, of 16·5°. The gain in an atmosphere saturated with water was practically the same as that in the ordinary atmosphere of the laboratory.

Mechanically dry urechitoxin is readily deprived of all water at 100° without its crystalline appearance being altered; but if a little more moisture be present than it naturally takes up from the air, that temperature will cause it to melt into a clear gum-like mass, from which it is very difficult to remove all moisture, unless it be first cooled and finely powdered.

Urechitoxin and its solutions are intensely bitter; half a c.c. of a water solution containing one part in 40,000 is strongly bitter, and a similar quantity of a solution of one in 100,000 has a distinct, somewhat astringent taste, but is hardly bitter. If left in contact with the lips or tongue for a short time, the poison produces a tingling, smarting sensation, and the affected parts feel swollen. If the smallest particle enters the nostrils it causes violent sneezing. It is very poisonous, as the facts given in my paper on its physiological action plainly prove; in one experiment less than one milligram of it subcutaneously injected proved fatal to a cat in 16 hours; in another an injection of three milligrams was fatal to a strong cat in one hour and a quarter.

Urechitoxin in excess, left in contact with water for several days, gives a solution containing one part of the poison in about 1,500 of the solvent; it is much more soluble in boiling water, in which the excess melts to a clear soft resin; the solution, on cooling and standing for a few hours, deposits a rather considerable crop of crystals, but permanently retains in solution about one-thousandth of its weight of urechitoxin. It may be well to mention here that whenever I speak of definite weights or proportions of "urechitoxin," the *dry* substance is referred to; the loose combination which it forms with about 9 per cent. of water, I distinguished as "Hydrated Urechitoxin."

The solubility of urechitoxin in spirit of various strengths, was determined by placing excess of the hydrated substance with the spirit in a corked flask which was frequently agitated. After standing for a day and two nights, the saturated solution was filtered off and a weighed quantity evaporated in a warm place, and finally heated in a water-oven as long as weight was lost. The temperature of the laboratory was about 15° during the preparation of the solutions. The following are the results obtained, the numbers being parts by weight of spirit required to dissolve one part of dry urechitoxin:—

965·0	spirit	containing	10	volumes	per cent.	of alcohol.
875·0	,,	,,	15	,,	,,	,,
585·0	,,	,,	20	,,	,,	,,
198·0	,,	,,	30	,,	,,	,,
65·0	,,	,,	40	,,	,,	,,
14·0	,,	,,	50	,,	,,	,,
4·3	,,	,,	60	,,	,,	,,
2·0	,,	,,	70	,,	,,	,,
1·4	,,	,,	80	,,	,,	,,

The saturated solutions in 60, 70, and 80 per cent. spirit were clear, but thick and syrupy. The poison is taken up to saturation by 70 and 80 per cent. spirit in a few minutes. The stronger alcoholic solutions deposit urechitoxin in a pseudo-amorphous form on addition of water, or even on exposure to the air. The solution formed by placing excess of dry urechitoxin in contact with spirit is much stronger than that resulting from the use of the hydrated substance, thus:

123 parts of 30 per cent. spirit dissolved 1 part of urechitoxin.
9·5 ,, 50 ,, ,, ,,

It is much more soluble in hot spirit; some of 30 per cent. was heated to its boiling point, and dry urechitoxin gradually added. It seemed as if it would be taken up indefinitely. As each portion was dropped into the spirit, it appeared to melt and blend rather than to dissolve. All the urechitoxin at hand was used, and a clear solution like strong gum-water obtained, which cooled without crystallising, but on standing a short time, crystals began to form, a stream of light liquid ascending from each one. In the course of a few hours the solution was converted into a magma of minute crystals, in which but little liquid was visible, and the tube might be inverted without anything escaping. In this experiment 1 part of urechitoxin was dissolved by 1·6 parts of the hot 30 per cent. spirit.

When dry urechitoxin in excess was left in contact with dry ether of 0·720 sp. gr., 1 part was dissolved by 565 of the solvent: but when the hydrated crystals were mixed with the same ether saturated with

water, 2,230 parts were needed for solution. Dry urechitoxin placed in benzene required 3,820 parts for solution. By chloroform the dry substance is taken up indefinitely, forming a soft resin-like mass; the hydrated poison is not so readily soluble, but is all but miscible. Amylic alcohol takes up dry urechitoxin as freely as does chloroform, but not so rapidly. When the hydrated crystals were mixed in excess with amylic alcohol, and the solution was filtered after standing for 24 hours, 1 part of urechitoxin was found to have dissolved in 3·7 parts of amylic alcohol.

Urechitoxin is exceedingly soluble in glacial acetic acid. If a strong solution be diluted with water, the poison is to a great extent immediately precipitated in a pseudo-amorphous condition; on standing, the dilute acid gradually deposits a further quantity in the crystalline form. The pseudo-amorphous urechitoxin left in contact with the weak acid, or with water or dilute spirit, gradually and entirely changes into ordinary urechitoxin, apparently without undergoing solution. I apply the term pseudo-amorphous to the non-crystalline urechitoxin obtained by fusing the crystals in water, or by evaporation of their solution in chloroform, &c., indeed to any urechitoxin in a non-crystalline state which by appropriate means can be changed into crystals, while I restrict the term amorphous to a substance resembling urechitoxin in many respects, but which I have entirely failed to convert into a crystalline form.

Pseudo-amorphous urechitoxin is reconverted into the ordinary urechitoxin by crystallisation from spirit, or by the prolonged contact of water or weak spirit in quantities far too small for its solution. Strong solutions of urechitoxin are very apt to deposit the pseudo-amorphous body, and it is so deposited from all solutions evaporated at a high temperature. Sometimes a drop or two of a solution of urechitoxin evaporated in the cold, for examination under the microscope, will give a residue in which no crystals can be detected; but by allowing a little water or very weak spirit to evaporate in contact with it, the residue will eventually be wholly converted into crystals. Pseudo-amorphous urechitoxin is easily powdered; the powder mixed with cold water becomes soft and aggregates together. If the mixture be well incorporated by vigorous stirring for a few minutes, and then filtered, a cold supersaturated solution is obtained, which in a few hours throws down the excess in the crystalline form.

Rapidly heated to between 170° and 180°, urechitoxin fuses without change; but if its temperature is gradually raised, it loses its crystalline appearance at about 150°, and at 160° is fully fused. By this slow heating it becomes slightly coloured, and its weight is diminished about three-quarters of a per cent.; it is, moreover, permanently changed into an amorphous form of the poison. A similar

change takes place to a small extent when its solutions are heated. This observation was made in recovering the urechitoxin used in determining its solubility, &c. This was done by crystallisation from hot 30 per cent. spirit, the mother-liquor from one operation being used to recover a subsequent quantity, and so on. Finally the mother-liquor was partially evaporated on a water-bath. On cooling, however, very few crystals formed; on still further evaporation and again cooling, no crystals were deposited. The liquor was now practically free from alcohol, yet very bitter. It was evaporated to dryness in a vacuum, leaving a resinous mass which refused to yield crystals to any treatment, and which perfectly resembled amorphous urechitoxin.

In strong cold aqueous hydrochloric acid urechitoxin dissolves freely to a colourless solution, which very speedily changes to yellowish-green, then becomes opalescent, and deposits crystals and more or less amorphous colouring matter. The reaction is complete in a few hours; if heat be applied it takes place immediately, but at the same time some other action is induced, in consequence of which a much smaller yield of crystals, or even none at all, is obtained. All bitterness is destroyed by this reaction. The crystals are much less soluble in spirit than urechitoxin; they crystallise in microscopic prisms and plates of a very light yellow colour, are tasteless, and give the urechitoxin colour reaction with greater brilliancy than the pure poison. I have not yet obtained it pure enough in quantity sufficient for analysis; but by using fuming aqueous hydrochloric acid, diluted with one volume of water and two volumes of absolute alcohol, as the solvent for the urechitoxin, and allowing sufficient time, a quantity of a crystalline substance uncontaminated with amorphous matter was obtained. This body I have named urechitoxetin; a description of it is given further on.

The strongly acid filtrates from the completed action of hydrochloric acid on urechitoxin contain nothing bitter, but hold in solution a body which immediately reduces boiling alkaline cupric solutions, causing precipitation of red cuprous oxide. By removal of the acid and subsequent evaporation in a vacuum, this body or mixture of bodies was obtained as a non-crystallisable treacly fluid, of a dark colour, and possessing no marked taste, but smelling of burnt sugar. It awaits further investigation.

A change somewhat similar to that produced by hydrochloric acid has been noticed to occur in water solutions of the poison left for a long time in closed vessels. For instance, a solution containing 1 part of urechitoxin in 10,000 of water remained unchanged for several weeks, but in the course of months a substance resembling the mould which so frequently forms in solutions of tartaric acid, was developed, and fine crystals precipitated. Neither the liquid nor the crys-

tals now had any bitter taste; the latter were comparatively insoluble in spirit, but gave the urechitoxin colour-reaction with great brilliancy.

Solutions of caustic potash and soda have no immediate effect on urechitoxin, but I have noticed that strong solutions of the poison in spirit which have been allowed to remain in an alkaline state for a considerable time lose their bitterness.

In strong nitric acid it dissolves readily and quietly to a light yellow solution, which gives off red fumes on being heated, at the same time becoming lighter in tint.

Colour-reaction.

Urechitoxin dissolves readily in strong pure sulphuric acid to a light orange-yellow solution having a tint of brown in it. If this solution be diluted with water, a dirty light yellow precipitate is thrown down. If, however, it is allowed to stand in a closed vessel, it gradually becomes of a redder and redder tint, passing through carmine to mauve, and finally into purple. These changes are much hastened by heat, and if the heat be continued the colour passes into a brown of great depth. Water added to the purple solution causes a dirty orange-coloured precipitate.

The colour changes are also produced by the addition of a small quantity of either of the following substances: nitrates, nitrites, chlorates, bleaching powder, bromine, and iodine. Ferrocyanide of potassium does not cause the colour changes, while ferricyanide brings the colours out slowly and without the brightness of tint produced by the reagents mentioned above. Chromates and bichromates change the yellow of the sulphuric acid solution to a very light yellow-green, the green gradually becoming stronger as the mixture stands, no doubt from the reduction of chromic acid.

Permanganate of potash, added cautiously, first bleaches the solution almost completely, then brings out a fine but not strong violet tint, which finally passes into a dirty brown colour.

I prefer nitric acid for the production of the colour changes, and as excess destroys all colour, I am in the habit of using an oxidising agent prepared by adding about a drop of nitric acid to 100 c.c. of sulphuric acid. If a drop of sulphuric acid is placed on 0·01 milligram of urechitoxin lying in a white basin, a yellow solution is produced, in which the changes of colour to mauve are distinctly seen on adding a minute drop of the oxidising liquid. Even 0·001 milligram will with careful manipulation give the reaction distinctly.

Tannic acid causes a white precipitate in a water-solution of urechitoxin (1 part in 1,500), which is redissolved on addition of potash

or acetic acid; but no precipitate falls if the solution be slightly more dilute. The tannate is very soluble in spirit. The various forms of the poisonous principle of the *Urechites suberecta* are much more soluble in water when contaminated with extractive matters derived from the plant than when in a pure state. These impure solutions give dense curdy precipitates with tannic acid. Every *bitter* water solution obtained from the plant, whether immediately or after the action of selective solvents, &c., I have found to give a precipitate with tannic acid, while no precipitate was formed in solutions devoid of bitterness.

Urechitoxetin.

The urechitoxetin prepared, as already described, by the action of alcoholic hydrochloric acid on urechitoxin, was carefully purified by repeated crystallisation from spirit, the final product being a quantity of light dull-yellow microscopic crystals with a silky lustre. They are readily and completely dried at 100°, and on exposing the dry crystals to the air for 48 hours, they take up but 0·2 per cent. of moisture. On analysis the purified and perfectly dry urechitoxetin gave the following results:—

	Obtained.		Percentage.	
Taken.	CO_2.	H_2O.	C.	H.
0·2147 gram	0·6091 gram	0·1642 gram	77·37	8·50
0·2580 „	0·7338 „	0·1959 „	77·57	8·44
0·1910 „	0·5423 „	0·1464 „	77·43	8·52

The mean percentage composition obtained is C 77·46, H 8·49, O 14·05, while the formula $C_{44}H_{58}O_6$ requires C 77·42, H 8·50, O 14·08.

Urechitoxetin has no marked taste, and is physiologically inactive: hence I have not investigated its properties to any great extent, and will merely mention a few of the more marked. It is practically insoluble in water and in weak spirit, nor does it dissolve to any large amount in spirit of 80 per cent., unless it be heated; much crystallises out as the solution cools. It appears to resemble urechitoxin in a certain proneness to pass into an amorphous modification. It dissolves in sulphuric acid to a light orange-yellow solution; if the solution is very strong, the colour is orange-red, but the increase in depth of tint is by no means proportioned to the amount dissolved: for after the redder tint is once reached, no marked gain in colour is seen on adding very much more urechitoxetin. On adding a minute quantity of nitric acid to the yellow solution, the same colour-changes are produced as urechitoxin similarly treated exhibits, but they are much clearer and brighter. If the oxidising agent be added to a strong solution, the increase of colour is very remarkable, the oxidised solution appearing

black and opaque except in a very thin stratum. Heat brings out the colour changes, and they also appear if the solution in sulphuric acid be allowed to stand in a closed vessel in the cold, but several days pass before the purple tint is reached. Water added to a fresh solution in pure sulphuric acid throws down a light canary-yellow precipitate, while if added after the purple colour has developed, the precipitate is dirty orange. Excess of oxidising agent quickly bleaches a sulphuric acid solution of urechitoxetin without showing the various colours with any clearness.

Amorphous Urechitoxin.

In the preparation of urechitoxin from leaves of *Urechites suberecta* dried at 100°, several samples of amorphous urechitoxin were obtained, great care was taken to remove all inactive matter, and as in their physiological and general chemical properties they closely resembled each other, I hoped they would prove to be of definite composition; analysis has, however, disappointed this expectation, the percentage of hydrogen found in different samples varying from 7·85 to 8·19, and the carbon from 62·02 to 64·46. Some recent experiments lead me to suspect that several bodies exist having the physiological activity of urechitoxin, some of them, no doubt, being ready formed in the plant, while others are produced by chemical changes. If this suspicion is correct, the samples of amorphous urechitoxin I have prepared are uncertain mixtures of two or more of these bodies.

Amorphous urechitoxin is, in appearance, intermediate between a resin and a gum; it has a light, dull yellow colour, and is readily powdered. It resembles urechitoxin in its toxic action, and is nearly, if not quite as poisonous; introduced into the mouth or nostrils it seems even more active, but this results simply from its greater solubility. In cold water it becomes soft; excess placed in weak spirit gradually melts into an oil-like liquid; it is miscible with strong spirit. It reacts with reagents in the same manner as does urechitoxin, but gives no *crystalline* product when acted on by hydrochloric acid, and perhaps its colour reaction is less vivid.

Urechitin.

This substance usually crystallises in long four-sided prisms, bounded at each end by two planes, but frequently more complicated forms appear. The crystals are transparent and colourless; they break very easily at right angles to their longest axis. As deposited from alcoholic solutions, the crystals contain 6 per cent. of water, which is readily driven off at 100°, no further loss resulting from

exposure to a temperature of 120° C. The anhydrous poison does not recover more than 1 per cent. of water if left in contact with cold damp air.

Urechitin contains no nitrogen. Analysis of the crystals after drying at 100° gave the following results:—

Taken.		Obtained.		Percentage.	
		CO_2.	H_2O.	C.	H.
Sample A.	0·2113 gram	0·5132 gram	0·1592 gram	66·24	8·37
	0·2671 „	0·6465 „	0·2002 „	66·01	8·33
	0·1480 „	0·3592 „	0·1123 „	66·19	8·43
Sample B.	0·1622 „	0·3952 „	0·1235 „	66·45	8·46
Sample C.	0·2887 „	0·7002 „	0·2176 „	66·15	8·38
	0·2905 „	0·7044 „	0·2182 „	66·13	8·35
	0·2474 „	0·6004 „	0·1850 „	66·19	8·31
Sample D.	0·2169 „	0·5277 „	0·1633 „	66·35	8·36
	0·2167 „	0·5263 „	0·1634 „	66·24	8·38

These figures show the four samples to be identical, and give a mean of C 66·22, H 8·38, and O 25·40, as the centesimal composition of urechitin. The formula, $C_{28}H_{42}O_8$, closely represents the analytical results:—

$$C_{28}H_{42}O_2 \text{ requires} \begin{cases} C & 66{\cdot}40 \\ H & 8{\cdot}30 \\ O & 25{\cdot}30 \end{cases} . \text{ Obtained} \begin{cases} C & 66{\cdot}22. \\ H & 8{\cdot}38. \\ O & 25{\cdot}40. \end{cases}$$

Urechitin in the solid form is tasteless, but its alcoholic solutions are equal to those of urechitoxin in bitterness, and it also resembles this substance in its toxic action and power. In cold water and cold spirit of less than 40 per cent. alcoholic strength, it is practically insoluble. Boiled in water it shows no sign of fusion; the liquid filtered hot and allowed to stand for a considerable time deposits a very small quantity of the poison in the crystalline state. Its solubility in various liquids was determined in the same manner as that of urechitoxin, with the subjoined results, the numbers being parts by weight of the solvent required to hold one part of urechitin (weighed after drying at 100°) in solution. The determinations were made at a temperature of about 16·5°.

1,580 spirit containing 50 per cent. of its volume of alcohol.
610 „ 60 „ „
190 „ 70 „ „
88 „ 80 „ „
35 very nearly absolute alcohol.

227 dry ether, sp. gr. 0·720.
420 same ether saturated with water.
140 amylic alcohol.
466 benzene.
2·7 chloroform.
167 boiling 30 per cent. spirit, the solution beginning to deposit crystals immediately on its temperature falling.

Urechitin differs from urechitoxin in not taking a pseudo-amorphous form; its solutions in the various menstrua already mentioned deposit it in the crystalline form whether they be evaporated slowly and at low temperatures, or on the water-bath. It is also precipitated in crystals on adding water to its solution in strong spirit or glacial acetic acid. It is freely soluble in this acid, though not to the same extent as urechitoxin, but it does not dissolve in dilute mineral acids.

When a small quantity, in a thin test-tube, was suddenly immersed in oil already heated to 220° it changed in appearance, but did not absolutely fuse; the tube was withdrawn, and when the temperature had risen to 260° it was again immersed; the poison now fused immediately, and on cooling was like colourless glass; it dissolved readily in hot strong spirit, and on evaporation the usual crystals of urechitin were obtained. Another portion was gradually heated; no alteration was visible until the temperature was over 180°, when the crystals began to colour here and there, but showed no signs of melting. When the bath was nearly 195° points of fusion were observed where the colouring had become most marked; the temperature was kept about 197°, and the change gradually progressed, while fumes were evolved which condensed on a cold surface to clear drops having a strong acid reaction. Ultimately the whole fused to a dark-brown mass, which was disposed to froth up as if gas were being generated in it. It was now removed from the oil-bath, and was found to have lost one-tenth of its weight. The cold fused mass was next treated with a few drops of cold strong spirit, in which it dissolved readily, with the exception of some crystals, which proved to be urechitin still unchanged by the heat. The alcoholic solution failed to yield crystals to any method of treatment, but on evaporation gave a substance closely resembling some of my samples of so-called amorphous urechitoxin; it was intensely bitter, and gave the colour-reaction well, but was less soluble than any other amorphous sample of the poison I have prepared.

Urechitin is acted on by strong aqueous hydrochloric acid much in the same way as urechitoxin; it is, however, not so freely soluble, and the solution on standing becomes much more strongly green. Crystals

are deposited which, as far as I have examined them, resemble those resulting from the action of the acid on urechitoxin; but the liquid from which the crystals have been deposited does not, after neutralisation, so readily reduce alkaline cupric solutions as does that from urechitoxin.

With sulphuric acid and oxidising agents, urechitin gives the same series of colours as urechitoxin, but they are hardly so bright, and are certainly inferior to those given by urechitoxetin. The difference is most marked in the fresh solution in pure sulphuric acid, which is of a brownish-yellow instead of the reddish-yellow colour of the urechitoxetin solution; the brown is very decided if the solution is strong. On diluting the freshly-made solution with water, a dirty green precipitate falls; if the water be added after the colour-changes have been developed by nitric acid, a precipitate similar in colour to that given by urechitoxin or urechitoxetin, viz., dirty orange, is thrown down. I have noticed that, by mixing sugar with urechitoxetin before trying its colour reaction, results very much like those yielded by urechitoxin and urechitin can be obtained.

That the various bitter poisonous substances described in this paper are glucosides I think is certain, but I do not consider sufficient data have been accumulated to allow a molecular formula to be assigned to either urechitin, urechitoxin, or urechitoxetin. The formulæ given in this paper are merely the simplest that express the numbers obtained by analysis, and it may well be that none of them represent the molecule, but that some much heavier formulæ differing but slightly in percentage numbers are correct.

The facts here recorded, together with others observed in the course of the research, lead me to think that if sufficient time were devoted to experimenting on *Urechites suberecta*, it might yield as many substances, and as confusing results as *Digitalis purpurea*. I have confined myself in this paper mainly to two definite crystalline bodies, and have left unenumerated several less definite though interesting substances, which have been noticed during the research. For instance, in one experiment on the preparation of urechitoxin, I got a small quantity of a substance as soluble in pure water as gum arabic, and possessing the toxic powers of the plant in a high degree; but having failed hitherto to obtain it in such a condition as would leave no reason to doubt that it was a definite compound and not a mixture, I do not think that honouring it with a name and detailed description, would tend to anything except confusion.

That the poisonous properties of *Urechites suberecta* are mainly due to urechitin is, I consider, established by the mode of its preparation, as it is unlikely that chemical change would be induced by the use of nothing more than water, alcohol, and a temperature never exceeding

38°. On the other hand, I have no doubt that urechitoxin is a product of chemical change from urechitin, a change wrought by the much more violent method of its preparation.

To guard against mistake, it may be well to add that whenever I speak of a substance as devoid of bitterness, tasteless, and so on, without mentioning whether it was in the solid form or in solution, it is to be understood that it was experimented with in both conditions.

I have succeeded in detecting these poisons when present in very minute quantities in complex mixtures by processes which their solubilities will suggest to any one familiar with the ordinary methods of detecting vegetable poisons in toxicological investigations; but as my experiments on the best methods of discovering them are not completed, I will not refer to their detection here.

In conclusion, I wish to state that the preparation of the various substances described was carried out in the Government Laboratory, Kingston, Jamaica, where most of the qualitative results were also worked out, while nearly all of the quantitative experiments were performed in the Research Laboratory, South Kensington, and that my best thanks are due to Dr. Frankland for kindly permitting me to work there.

XXX.—*Note on a New Manganese Reaction.*

By J. B. Hannay, F.R.S.E., Assistant Lecturer on Chemistry in The Owens College, Manchester.

While examining a new mineral (*Journ. Min. Soc.*, No. 5) containing manganese, I noticed that when a solution of manganous salt in strong nitric acid is warmed, with addition of crystals of potassic chlorate, the whole of the manganese is precipitated as manganous manganate. When a salt of iron is present, the manganese is still precipitated, but in combination with the iron, as a double manganate of iron and manganese of the formula,—

$$2Fe_2(MnO_4)_3.MnO.MnO_3.12H_2O; \text{ or } Fe_2(MnO_4)_3MnO_2.6H_2O.$$

The manganese dioxide precipitated when there is no iron present seems to be identical with the mineral *pyrolusite*, as it is in crystalline plates which in mass are black, but in small quantity, as seen under the microscope, steel-grey. The thinner plates are transparent, having a reddish-purple colour, and the compound contains no water. On

ignition it is converted into manganoso manganic oxide, which often retains the plate form of the original dioxide.

The above reaction seemed to offer an easy method of preparing metallic manganates, but as far as I have examined, no other metals are precipitated with the manganese under the same conditions, those tried being aluminium, barium, bismuth, cadmium, calcium, chromium, cobalt, copper, lead, magnesium, mercury, nickel, strontium, and zinc. When dry chloride of manganese is treated with strong nitric acid and warmed, the chloride is rapidly transformed into nitrate, with evolution of nitryl and nitrosyl chloride; in fact so rapidly does this take place, that the effervescence is like that produced by a readily oxidisable metal dissolving. It was found that other chlorides behave in the same manner, notably those of cobalt and nickel. It would seem that when chloride of manganese is treated with strong nitric acid and chlorate of potassium, only those portions which are converted into nitrate are precipitated, as the precipitation takes much longer than when either nitrate or sulphate is used. The compound is a remarkably stable body, being insoluble in nitric and sulphuric acids, whether dilute or concentrated, and unaffected by caustic alkali. Hydrochloric acid acts readily upon it, and reducing agents, such as ferrous sulphate, stannous chloride, sulphurous acid, and phosphorous acid rapidly decompose it, the ferric hydrate obtained by the action of ferrous sulphate being yellow in colour. Sulphurous acid acts upon the substance very rapidly, but attacks the ferric compound first, leaving the manganic dioxide, which afterwards slowly disappears in consequence of the well known reaction for the production of dithionates. The decomposition of the ferric compound is represented as follows:—

$$Fe_2(MnO_4)_3 + 6SO_2 = Fe_2(SO_4)_3 + 3MnSO_4.$$

Ferric sulphate is formed, but if excess of sulphurous acid be added, the ferric salt is reduced, not at once, but in a few minutes, as is seen by the yellow colour slowly disappearing. When the quantity of sulphurous acid required for the above decomposition is added to the compound, and the liquid quickly filtered, the required quantity of manganese dioxide is found upon the filter, as shown by the following numbers:—

Substance taken.....	0·5213 gram	
MnO_2 found	0·0660 „	= 12·66 p.c.
Calculated		13·10 „

This shows that the reaction is

$$Fe_2(MnO_4)_3.MnO_2.6H_2O + 6SO_2 = Fe_2(SO_4)_3 + 3MnSO_4 + MnO_2 + 6H_2O.$$

It was noticed that in all the reactions in which manganese dioxide was set free, the substance rapidly collected into little nodules, which possessed a considerable degree of coherence. This property of the dioxide is seen very strongly developed in the nodules which collect at the sea bottom at great depths, where all the calcium and other compounds which were associated with it are dissolved out, leaving the manganese free, it being seldom or never found as sand, but always in the form of nodules. I am trying the experiment of adding a few drops of sulphurous acid and some of the manganese compound every few days to a large vessel of sea water, to find whether large coherent nodules may not be thus artificially grown. They are already of a considerable size.

It was found that a large excess of iron makes little or no difference in the composition of the precipitate, the following two analyses being made from samples prepared from solutions containing in one case a moderate excess of iron, and in the other about ten times as much iron as manganese.

	Found.		
	I.	II.	Calculated.
Fe_2O_3.....	22·87	24·38	24·09
MnO_3	46·18	46·34	46·54
MnO_2	14·22	13·51	13·10
H_2O	15·99	16·14	16·27
	99·26	100·37	100·00

The proportion of MnO_3 to MnO_2 in the samples was found by estimating the oxygen by several different methods:—1st, by ignition; 2nd, by the amount of chlorine evolved on dissolving the substance in hydrochloric acid; and 3rd, by solution of the substance in presence of ferrous sulphate, and estimation of the amount of ferric salt formed. Before carrying out the first estimation, the amount of water contained in the substance was determined, and was found in three samples to be 14·26, 16·50, and 15·89 per cent. respectively. The substance is exceedingly hygroscopic, holding from 3 to 4 per cent. of moisture, even at 160°, and it is only on continued heating at 180° that no further loss of weight occurs. That the total loss is moisture was proved by weighing the evolved water in sulphuric acid; besides the compound re-absorbs the total quantity on exposure to air for a few hours. Although the substance is very hygroscopic, it is (as its insolubility would argue) by no means deliquescent—it does not even cake in moist air, but remains dry and powdery. Before analysis it was dried over calcic chloride, because if left long over oil of vitriol it lost some moisture. On ignition a total loss of from 29·5 per cent. to 30·69 per cent. was suffered by different samples, and if we deduct

from this 15·27 per cent. for moisture, we have 13·83 per cent. of oxygen driven off, which agrees pretty well with the decomposition—

$$3[Fe_2(MnO_4)_3MnO_26H_2O] = 3Fe_2O_3 + 4Mn_3O_4 + 17O + 18H_2O,$$

which requires 13·65 per cent. The oxygen estimated by ferrous sulphate and chlorine gave quantities varying from 14 to 16 per cent., the required amount being 16·86 per cent. On doing a large number of analyses of different samples, it soon became evident that the substance was by no means constant in composition, but was mixed with varying quantities of manganous manganate. The reason of this variation is not yet clear, because two samples prepared from the same chemicals, and precipitated in apparently the same conditions, did not agree in composition. The compound when pure is similar in appearance to the precipitated dioxide, and appears under the microscope to be composed of thin flexible plates, of a purple-brown colour,—a colour also seen in the thin films which adhere to the vessel in which it is formed. The thinner the plate the more purple is it; the thicker, the redder does it appear. Light passed through the filter shows, when examined by the spectroscope, no well defined selective absorption, the blue being merely gradually stopped out. As in some of the first experiments tried, all the iron was precipitated out of the solution when excess of manganese was used, it appeared to afford a good method of separating iron from other metals, especially aluminium, without the use of alkali; but subsequent experiments have shown me that the reaction is too indefinite, and the conditions under which complete precipitation takes place are too changeable to admit of its use as a process in analysis. As illustrating the uncertainty of this reaction, I add a table of several precipitations:—

Fused.			Precipitated.	In solution.
$Mn(NO_3)_2$.	Fe_2O_3.	Al_2O_3.	Fe_2O_3.	Fe_2O_3 and Al_2O_4.
2·2640	0·2825	0·3017	0·2820	0·3025
2·2640	0·2655	0·2600	0·2025	0·3235
2·2640	0·1500	0·2100	0·1385	0·2220
2·2640	0·1000	0·1000	0·0938	0·1065
2·2640	0·3000	0·3000	0·2265	0·3735

These samples are sufficient to show that the separation is incomplete (not in every case, for in some no trace of iron was found in solution), and cannot be used as a process. I have made a very large number of experiments, raising and lowering the temperature, adding more or less acid, adding acid more or less concentrated, and altering the proportion of the three basic constituents, but have not yet suc-

ceeded in finding any cause for the vagaries of the precipitation. When too high a temperature is used, the mixture explodes, but it appears to be best precipitated near the point of the decomposition of the chloric acid. I may say that none of the other oxides of chlorine cause this reaction, those tried being perchloric acid, chlorous acid, and hypochlorous acid. An observation made may as well be recorded here. It is said that manganous nitrate crystallises only in needles, which turn brown on exposure to air; but I have found that a solution of manganous nitrate in nitric acid crystallises in beautiful, transparent, colourless crystals, some of them simple forms of the monoclinic system, and some modified therefrom (double oblique pyramids being very common), which, although deliquescent, are otherwise perfectly stable in air, and not prone to oxidation.

The iron compound seems to be identical in composition with a form of "wad" found at Austerlitz, N.Y., analysed by Beck, who finds Fe_2O_3, 22·00; manganic oxide, 58·50; and water, 17·00 per cent.; this agreeing very well with my analysis. I have obtained radiating star-like crystals of both the precipitated compounds, which look very like the ordinary crystalline form of pyrolusite. Of course, as will be understood from what I have said, compounds are formed containing any higher multiple of the manganous manganate; but I have considered these to be mixtures of the two ultimate bodies which I have described.

XXXI.—*High Melting Points.* Part IV.

By Thomas Carnelley, D.Sc. (Lond.), Assistant Lecturer on Chemistry in The Owens College.

As I pointed out in my first paper on this subject (*Chem. Soc. J.*, 1876, i, 489), the specific heat method for determining high melting points gives results which, for temperatures up to 400° or 500° C., are somewhat too high. I have recently submitted the process to a complete investigation as to the cause of this error, and I have likewise determined the melting points of a great number of additional bodies, the results of which are detailed in the present paper.

The error mentioned above I have proved to be due to two sources:—

(1.) *The Overheating of the Suspending Wire of the Crucible.*—As described in Part I, the platinum crucible used in the determinations

is suspended in the flame of the Bunsen lamp or blowpipe by means of a platinum wire. This wire becomes over-heated, and consequently has a higher temperature than the crucible, thus making the melting point of a given substance too high. Up to within quite recently it was thought that the error due to this cause would be inappreciable, on account of the small weight of the wire compared with that of the crucible; but I have since found that it does exert a slight but important influence in raising the melting point, and that in proportion as the melting point of the body is low. This error has been obviated by using as thin a wire as possible consistent with strength sufficient to support the crucible. Such a wire is considerably thinner than that formerly employed, so that the error due to its being over-heated has no appreciable effect on the result.

The error introduced by the previous use of too heavy a wire has been determined, and a correction made in the results obtained in Part I.

(2.) *The Value of the Calorimeter.*—In my first communication (*vide supra*) the value of the calorimeter was found by taking the sum of the products of the weights of the copper vessel, glass, and mercury of thermometer into their respective specific heats, while in Part III (*ibid.*, 1877, i, 381) I took a value which was obtained by heating the crucible in an air-bath to a known temperature, and then dropping it into the calorimeter containing a known weight of water. This gave a value considerably higher than that found by the first method, and consequently raised the melting points of the 28 salts enumerated in Part I by from 9° in the case of silver nitrate to 40° in that of sodium sulphate, thus increasing the difference between the melting points as found by the specific heat method and those which had been determined directly with a mercurial thermometer. Since that time I have subjected the determinations of the value of the calorimeter to a careful investigation, which has led me to the conclusion that the value as determined by the second of the above methods is too high, owing to a considerable loss of heat which the crucible suffers between its removal from the air-bath and immersion in the water of the calorimeter, and also that the value as found by the first method, though a little too low, is nearly correct.

The method I now adopt for this determination is as follows:—

Several salts, the melting points of which have been very carefully determined with a mercurial thermometer, are taken and submitted to the same treatment as in the determination of a melting point by the specific heat process, and then from the formula—

$$M \times S \times (T - \theta) = (W + w)(\theta - t).*$$

* M = weight of crucible; S = specific heat of platinum from 0 to T; T = melt-

in which all the values are known except (w), the influence of the calorimeter may be found. By this method the following results were obtained (p. 276).

Though the different values of the calorimeter obtained above vary somewhat largely (viz., 5·4 to 13·3), yet the melting points as determined by the use of the mean value 9·8 agree very nearly with one another, and with those found with a thermometer. The value 9·8 is almost the same as that obtained by adding together the products of the weights of the copper vessel, glass, and mercury of thermometer with their respective specific heats, viz., 9·487 grams, being a little higher, as would *à priori* be expected. The value 9·8, therefore, is sufficiently correct for all practical purposes.

The following is a list of the salts, the melting points of which I have so far determined by the specific heat method, using 9·8 as the value of the calorimeter, and as fine a suspending wire as possible. Where not otherwise stated, the melting points as determined with a thermometer are corrected:—

Salt.	M.-p. specific heat method.	Mean.	M.-p. as found by thermometer or means other than specific heat.
AsI_3.....	—	—	146 (Carnelley).
H_3BO_3.....	187 186	186	184 (Carnelley).
$AgNO_3$.....	215 219	217	219 (*Watts's Dictionary*); 198 (Pohl, *Jahresb.*, 4, 59; not stated whether corrected or not. Determined by covering the bulb of a thermometer with a layer of fused salt, and then placing in an empty tube and heating); 218°, resolidifies at 212° (Carnelley).
$C_2H_2O_4$.....	203 204	203	200 (Carnelley). Anhydrous oxalic acid.
$HgBr_2$.....	243 242 240	242	223 (Oppenheim, *Clarke's Constants of Nature*, but reference there given incorrect); 244 (Williams); 244 (Carnelley).
$LiNO_3$.....	255 276 264 274	267	264 (Carnelley).
Tl_2CO_3.....	273 274	273	269 (Williams); 272 (Carnelley).
$HgCl_2$	292 295	293	287 (Williams); 288 (Carnelley).
SbF_3	301 300 278 291	292	

ing point of the salt as found by a mercurial thermometer; t = initial and θ = final temperature of the calorimeter; W = weight of water; and w = value of calorimeter in grams of water.

Salt.	W.	Mean.	M.-p. as found by mercurial thermometer.		M.-p. as found by specific heat method, using $w = 9 \cdot 8$.	Mean.	Difference between the M.-p. as found by thermometer and specific heat method.
			Uncorrected.	Corrected.			
$AgNO_3$	(1.) 12·7 (2.) 8·7	10·7	211° C.	218	(1.) 215 (2.) 219	217° C.	− 1
$HgBr_2$	(1.) 10·6 (2.) 13·3 (3.) 11·7	11·9	234	244	(1.) 243 (2.) 242 (3.) 240	242	− 2
Tl_2CO_3	(1.) 8·8 (2.) 8·4	8·6	261	272	(1.) 273 (2.) 274	273	+ 1
$HgCl_2$	(1.) 7·0 (2.) 5·4	6·2	276	288	(1.) 292 (2.) 295	293	+ 5
$NaNO_3$	(1.) 12·2 (2.) 12·1 (3.) 10·4	11·6	303	319	(1.) 315 (2.) 315 (3.) 318	316	− 3
	Mean ..	9·8				Mean error..	± 2·4°

Salt.	M.-p. specific heat method.	Mean.	M.-p. as found by thermometer or means other than specific heat.
$NaClO_3$	302 303	302	
$NaNO_3$	315 315 318	316	314 (Braun, *Pogg. Ann.*, 154, 190); 310 (Person, *Ann. Chim. Phys.*, 1847, xxi, 329); resolidifies 313 (Schaffgotsch, *Pogg. Ann.*, cii, 293); 319 (Carnelley).
KNO_3	338 338 342	339	342 (Brann, *Pogg. Ann.*, cliv, 190); 339 (Person (*Ann. Chim. Phys.*, xxi, 329); resolidifies 338 (Schaffgotsch, *Pogg. Ann.*, cii, 293).
$KClO_3$	357 362 357	359	334 (Pohl, *Jahresb.*, iv, 59), *vide* under $AgNO_3$. It cannot be correct, since $KClO_3$ melts above KNO_3. It is not stated whether 334° C. is the corrected temperature or not; if not the correction would make it several degrees higher.

Salt.	M.-p. Specific heat method.	Mean.	Salt.	M.-p. Specific heat method.	Mean.
PbI_2.....	387 390 381 374 385	383	$Tl_{12}V_{14}O_{41}$.....	398 413 415 409 403	408
$Ag_4V_2O_7$	377 386 386	383	$Ba(ClO_3)_2$	415 404 422	414
$Ag_{12}V_8O_{26}$	384 384	384	$TlVO_3$	425 423	424
$Tl_{12}V_8O_{26}$*	399 398 386 385	392	AgBr.....	437 427 423 423	427
$ZnBr_2$	398 393 391	394	TlCl‡.....	430 432 422 425	427
CdI_2.....	404 404	404	Ag_3VO_4§	485 421 408 565	403 to 565
$Tl_{12}V_{10}O_{31}$	402 406	404			
Hg_2Br_2†	*a.* 405	*a.* 405			

* Two different samples.

† Did not melt, but volatilised. The temperature given represents that at which all the salt had volatilised without melting. It therefore melts above 405°.

‡ Above 260°, Crookes (*Chem. Soc. J.*, 1864, 139).

§ Very difficult to see when it melted. Appeared to soften and melt gradually.

Salt.	M.-p. Specific heat method.	Mean.	Salt.	M.-p. Specific heat method.	Mean.
Cu_2Cl_2	429	434	AgI‡	526	527
	437			527	
	437			527	
TlI	437	439	$CdCl_2$	548	541
	440			531	
	441			544	
LiI	451	446		543	
	444		LiBr	548	547
	442			547	
ZnI_2	444	446	$Ca(NO_3)_2$	572	561
	447			554	
	447			563	
AgCl	453	451		556	
	446		$Na_2B_4O_7$	553	561
	450			561	
	453			568	
$Tl_4V_2O_7$	451	454	$NaVO_3$	572	562
	456			561	
	459			553	
	451			564	
TlBr	461	458	$Na_{12}V_8O_{26}$	559	562
	458			563	
	454			564	
$AgPO_3$*	484	482	Tl_3VO_4	568	566
	473			565	
	487			565	
	482		$CdBr_2$	566	571
$CuCl_2$	511	498		570	
	491			577	
	496		$Ba(NO_3)_2$	592	593
	493			594	
$PbCl_2$†	502	498	Bo_2O_3§	571	577
	501			585	
	499			575	
$PbBr_2$	500	499	$2(NaVO_3)V_2O_5$	571	581
	502			591	
	496			580	
SrI_2	515	507	$Ag_4P_2O_7$‖	584	585
	505			587	
	500			583	
CdF_2	533	520	LiCl	601	598
	513			605	
	515			589	
	518			597	

* Prepared by precipitating $AgNo_3$ with an excess of $NaPO_3$, the latter being obtained by fusing microcosmic salt. Became black on heating; fused mass, after cooling in water, was yellow, probably due to conversion into Ag_3PO_4.

† 580 (Braun, *Pogg. Ann.*, cliv, 190).

‡ 450 (Rodwell, *Chem. News*, xxxi, 4). This was simply deduced from the fact that it melted somewhat above the melting point of zinc, 412° C.

§ Difficult to see, as it appeared to soften and then melt.

‖ Became black on heating; fused mass, after cooling in water, was yellow, probably due to formation of Ag_3PO_4.

Salt.	M.-p. Specific heat method.	Mean.	Salt.	M.-p. Specific heat method.	Mean.
Cu_2I_2	598	601	Li_2CO_3	699	695
	605			698	
$NaPO_3$	616	617		687	
	615			697	
	620		$MgBr_2$	At same point as Li_2CO_3	695
NaI	630				
	618				
	635	628	KBr	697	699
	634			698	
	633			702	
	620		NaBr	700	708
$SrBr_2$	620			713	
	625	630		720	
	641			702	
	636			704	
CaI_2	631	631		712	
	631		$MgCl_2$	At the same point as NaBr	708
Tl_2SO_4	630	632			
	636				
	631				
KI*	638	634	RbCl	710	710
	628			711	
	633		$CaCl_2$	720	719
	635			719	
	637			718	
$Ca(VO_3)_2V_2O_5$	638	637		720	
	636		$2(Pb_2V_2O_7)PbO$	721	731
RbI	640	642		739	
	647			733	
	639		KCl†	728	734
$Sr(NO_3)_2$	646	645		744	
	645			732	
	645			734	
$Na_4V_2O_7$	657	654	ZnF_2	Melts at same point as KCl	734
	652				
Ag_2SO_4	656	654			
	656				
	651	658	RbF‡	740	753
V_2O_5	659			766	
	658			753	
$CaBr_2$	695	676	MoO_3§	761	759
	663			756	
	676			759	
	673				
	675				
RbBr	679	683			
	688				
	683				

* 666 (Braun, *Pogg. Ann.*, cliv, 190).
† 730 (Braun, *Pogg. Ann.*, cliv, 190).
‡ Very deliquescent. Melting point very difficult to see.
§ White; became very dark on heating (dark green?) and then whitish-yellow.

Salt.	M.-p. Specific heat method.	Mean.	Salt.	M.-p. Specific heat method.	Mean.
NaCl*	789		$SrCl_2$¶	819	
	765			829	825
	770			826	
	772	772	K_2CO_3**	834	
	775			836	834
	777			832	
	757		Na_2SO_4††	863	
	772			863	861
KF	791			856	
	785	789	$Pb_5(VO_4)_3Cl$‡‡..	—	*a.* 802
	792		$Pb(VO_3)_2$	—	*a.* 849
$Pb(PO_3)_2$†	800	800	Ag_3PO_4	—	*a.* 849
	800		Li_3PO_4	—	*a.* 857
LiF‡	778		$Ba_2V_2O_7$	—	*a.* 863
	819	801	Na_3VO_4	—	*a.* 866
	793		$Na_4P_2O_7$	—	*a.* 888
	816		NaF	—	*a.* 902
$Pb_2P_2O_7$§	799		CaF_2	—	*a.* 902
	805	806	SrF_2	—	*a.* 902
	815		BaF_2	—	*a.* 908
$BaBr_2$	809	812	Cu_2F_2	—	*a.* 908
	815		MgF_2	—	*a.* 908
Na_2CO_3‖	823		BiI_3	—	decomposes
	807	814			
	810		BiF_3	did not melt at 804, probably decomposed.	
	816				
Li_2SO_4	820				
	815	818			
	821				
	818				

* 960 (Braun, *Pogg. Ann.*, cliv, 190).
† Becomes dark grey on heating, and white again at a red heat.
‡ The melting point was very difficult to see.
§ Undergoes some change on heating, as $Pb(PO_3)_2$.
‖ 920 (Braun, *Pogg. Ann.*, cliv, 190).
¶ 910 (Braun, *Pogg. Ann.*, cliv, 190).
** 1150 (Braun, *Pogg. Ann.*, cliv, 190).
†† 1280 (Braun, *Pogg. Ann.*, cliv, 190).
‡‡ Artificial vanadinite. (*a*) prefixed to a number means that it melts above that temperature.

In the case of some of the salts mentioned in the above table, it was impossible to determine the melting point in the ordinary way, as they decomposed into metallic oxide and free acid, owing to the presence of moisture in the air and from combustion of the lamp flame. The method adopted, therefore, was to heat the salt in question with two or three others of known melting point on a sheet of platinum, and observe between which two it melted. By this means the salt did not appear

to decompose till after fusion, for the temperature of fusion was much sooner reached than when the large platinum crucible was used.

In the present paper I simply give the melting points I have so far determined, and in a week or two I hope to publish some very interesting theoretical results which I have deduced from them, one of the most important of which is that "in simple binary compounds, if one of the elements remains the same, then the melting point is a periodic function of the atomic weight of the other." I also hope to point out a method by which many unknown melting points may be predicted.

XXXII.—*On the Determination of High Boiling Points.*

By T. Carnelley, D.Sc., and W. Carleton-Williams, Assistant Lecturers on Chemistry, Owens College.

In conducting a research on certain high boiling hydrocarbons we strongly felt the want of some method for determining with ease and with merely an approximate degree of accuracy the boiling points of those bodies which volatilise at temperatures too high to be measured by the mercurial thermometer. As it is probable that the same difficulty may have been experienced by others, it seemed to us that an account of the plan we adopted would not be uninteresting.

Our method consists in noticing whether certain salts melt on exposure to the vapour of the boiling substance. Now as the melting points of a large number of metallic salts have been determined by one of us (see preceding paper), we can in this way ascertain within certain limits the temperature of the boiling point in question.

For temperatures below 500° the substance may be boiled in an ordinary distillation flask, provided with a perforated cork, through which pass several capillary tubes containing salts which melt at known temperatures. If the substance boils above 500°, it is necessary to heat it in a tube of hard glass by means of the blowpipe. The tube is held in a slanting position, and passes through a hole in the centre of a piece of sheet iron, in order to protect that portion which is above the boiling liquid from the action of the flame. The capillary tubes containing the salts must also be made of hard glass. When the vapour of the boiling substance attacks glass, it is often difficult to observe whether the salts have melted. In this case it is advisable to protect the tubes from corrosion by inclosing them in thin glass sheaths.

In the following table the boiling points determined by our method (Column III) are compared with the actual temperature (Column IV) measured by a mercurial thermometer, the stem of which was completely immersed in the vapour of the boiling liquid. Column I contains the names of the substances, and II the salts used in determining the boiling point. The symbol + is used to indicate that the salt melts, and — to show that no change takes place.

I.	II.	III.	IV.	Remarks.
$HgCl_2$	+ $NaClO_3$ — $NaNO_3$	302—316°	303°	In *Watts's Dictionary* the b.-p. given is 295°.
$HgBr_2$	+ $NaNO_3$ — KNO_3	316—339	319	
$SbCl_3$	+ $AgNO_3$ — HgI_2	218—241	221	According to Kopp, 223°. Capitaine, 230°.
Diphenyl.....	+ $HgBr_2$ — Tl_2CO_3	244—278	257	
Benzoic acid, m.-p. 121° ..	+ $HgBr_2$ — Tl_2CO_3	244—278	249	Kopp (*Jahresb.*, viii), m.-p. 121·4; b.-p. 249·2.

Now on referring to the list of melting points previously mentioned, it will be seen that but few of the salts melt below 300°, consequently we cannot bring the boiling point within such narrow limits as we can for higher temperatures. It must also be remembered that the method is only meant to be used for temperatures for which a mercurial thermometer cannot be employed, and in cases where merely an approximate knowledge of the temperature is required. The accuracy can obviously be increased by determining the melting points of a larger number of salts.

The following numbers show that good results are obtained at high temperatures:—

I.	II.	III.	Remarks.
Hg	+ $NaNO_3$ + KNO_3 — $KClO_3$	339—359°	The boiling point of Hg has been carefully determined by Regnault (*Jahresb.*, xvi, 70) and by Dulong and Petit. The former found it to be 357·25°, and the latter 360°.
Sulphur purified by recrystallisation from carbon disulphide	+ TlI + ZnI_2 — AgCl	446—451	Regnault (*Relation des Expériences, &c.*, ii, 527) states the b.-p. of sulphur to be 447°. Hittorf gives the same number, but according to Dumas sulphur boils at 440°. Most of the determinations of the boiling points of S and Hg appear to have been made by means of the iodine pyrometer.

We have successfully applied our method in fractionating high boiling hydrocarbons, and in determining the boiling points of the following substances:—

I.	II.	III.	Remarks.
Anthracene, the specimen melts at 212·5°	+ KNO_3 − $KClO_3$	339—359°	Graebe and Liebermann (*Lieb. Ann.*, Supp. vii, 264) state that anthracene boils a little above 360°, but they do not describe how they measured the temperature.
HgI_2	+ $NaNO_3$ + KNO_3 − $KClO_3$	339—359	Prepared by triturating iodine and mercury in presence of a small quantity of alcohol.
AsI_3.....	+ $ZnBr_2$ − $Ba(ClO_3)_2$	394—414	Prepared by subliming a mixture of As and iodine.
$BiCl_3$	+ $Ba(ClO_3)_2$ + TlCl − TlI	427—439	Two specimens, one prepared by dissolving bismuth in aqua regia, the other by burning the metal in chlorine gave the same results. The chloride decomposes slowly on long continued boiling; chlorine is evolved, and golden needle-shaped crystals are deposited.
$BiBr_3$	+ AgCl + $Tl_4V_2O_7$ $AgPO_3$ − $PbCl_2$ − AgI	454—498	Prepared by the action of bromine on the pure metal.
SbI_3.....	+ PbI_2 + $Ba(ClO_3)_2$ − TlCl − AgCl	414—427	Prepared by heating a mixture of iodine and antimony. The crude product was purified by sublimation over metallic antimony. The iodide melts at 171° (corr.), and decomposes slightly when boiled. The vapour has an intense dark red colour.
$ZnBr_2$	+ RbBr + Li_2CO_3 − KBr − NaBr	695—699	
$PbCl_2$	+ Na_2SO_4	Above 861	Prepared in the wet way; recrystallised from boiling water; attacks glass.
$PbBr_2$	—	—	Does not boil before the blowpipe. Attacks glass very rapidly.
$CdCl_2$	+ Na_2SO_4	Above 861	Two specimens gave the same results; a deposit separates out on boiling.

For the following substances a higher temperature is obtained by immersing the salts in the boiling liquid instead of in the vapour, whereas in the instances given above, the same result was got in both cases.

I.	In vapour. II.	In vapour. III.	In liquid. IV.	In liquid. V.	Remarks.
$ZnCl_2$	+ V_2O_5 + $CaBr_2$ – $RbBr$ – KBr	676—683	+ KBr + $NaBr$ – $CaCl_2$	708—719	Attacks glass, and becomes turbid on boiling.
$TlCl$..	+ Li_2CO_3 + $NaBr$ – $CaCl_2$ – KCl	708—719	+ $CaCl_2$ – $2(Pb_2V_2O_7)PbO$ – KCl	719—731	Melts to a pale yellow liquid, which changes to a cherry red, and finally again turns yellow.
TlI ..	+ $NaCl$ + $Pb(PO_3)_2$ – $Pb_2P_2O_7$ – Na_2CO_3	800—806	+ $Pb_2P_2O_7$ – Na_2CO_3	806—814	Decomposes slightly on boiling.
Cd ..	+ KCl + MoO_3 – $NaCl$ – Na_2CO_3	763—772	+ MoO_3 NaCl begins to melt.	772	Deville and Troost (*Compt. rend.*, xlix, 240) give 860° as the boiling point of Cd, but how this number was obtained is not clearly stated.

We hope shortly to determine the boiling points of potassium, sodium, magnesium, thallium, and other metals, with special reference to their bearing on Mendelejeff's law of the periodicity of the elements.

XXXIII.—*On the Action of Bromine upon Sulphur.*

By J. B. Hannay, F.R.S.E., Assistant Lecturer on Chemistry in the Owens College, Manchester.

In a former paper (*Chem. Soc. Journ.*, vol. xi, 1873, p. 823) I endeavoured to show, by an examination of the properties and decomposition of sulphur bromide, that, if such a compound existed, the elements were united by the faintest possible ties, and were not, as in sulphur chloride, united in their combining proportions to form a definite stable compound. The small quantity of heat evolved on mixing the two bodies is in itself sufficient to show that the chemical action is very slight, when we consider the energetic nature of either of the two elements. It was also mentioned in the above paper, that, on adding metallic arsenic to the mixture of bromine and sulphur, a new com-

pound was formed, and as my observations on this point are now complete, and as I have collected a considerable mass of data relating to the action of bromine upon sulphur, I beg to lay the results before the Society.

First, as to the general action of bromine. On treating ordinary flowers of sulphur with bromine, it was noticed that a portion of the sulphur remained insoluble (that is why in my former paper I said the liquid was filtered), and on examining this insoluble portion, it was found to be entirely composed of prismatic or insoluble sulphur, which is always present in small quantities in flowers of sulphur. With roll sulphur this insoluble substance did not occur. To determine whether the amount left undissolved by bromine was the same as that by carbon disulphide, the following experiment was tried:—5 grams of flowers of sulphur were weighed out, and added in small quantities at a time to about 20 grams of bromine, in order to prevent any great rise of temperature, as it was found that hot bromine dissolved the insoluble sulphur; the liquid was filtered, the filter washed with carbon disulphide, and the sulphur weighed. Its weight was found to be ·0040 gram, equal to ·08 per cent. of the sulphur used. On treating 5 grams of the same sulphur with carbon disulphide, it was seen that very much more would be left insoluble, but it was found that on pulverising in an agate mortar and washing repeatedly with the disulphide, the amount became much smaller. It appears that some of the globules in ordinary flowers of sulphur are coated with insoluble sulphur, which retards or prevents the solvent action of the disulphide, the pulverisation allowing the disulphide to penetrate into the little spheres. When it appeared that no further solvent action was going on, the insoluble sulphur was filtered off and weighed, and was found to weigh ·006 gram, or 0·12 per cent. of the sulphur used. This result is, as would be expected, higher than the bromine result, but it shows that in the cold the action of bromine upon sulphur partakes more of the nature of solution than of chemical action. When it was thus found that insoluble sulphur was not readily acted upon by bromine, it seemed important to determine by some physical method whether or not the bromine in sulphur bromide were really combined or free. My former experiment showed that at temperatures above 80° the bromine was free, but at temperatures below the boiling point an experiment with phosphorus seemed to show that some kind of combination was in force, but there was no definite information on the subject. I found, however, that if a beam of light be passed through the stratum of vapour and air overlying the surface of the liquid, and this beam be examined spectroscopically, the absorption spectrum of bromine vapour (lately mapped by Professors Roscoe and Thorpe, *Phil. Trans. Roy. Soc.*, vol. clxvii), was distinctly visible. On lowering

the temperature, the spectrum was still visible, though much fainter. When the temperature was lowered to 0°, the spectrum failed to appear; but on placing some other liquid in a long tube, closed at both ends with glass plates, laying it on its side, and passing the beam of light, the absorption spectrum again became visible. This plainly shows that the disappearance of the spectrum was owing to the lowered vapour-tension of the bromine, and not to its complete absence. On adding an excess of sulphur to the liquid and heating till it was all dissolved, the mixture failed to show the absorption spectrum of bromine at ordinary temperatures, except with a very thick stratum, and at lower temperatures it was invisible, even when a tube 1 meter long was employed. It appeared that a comparison of stability might thus be instituted between different mixtures of sulphur and bromine, and the following method was used. A tube 0·5 meter long and closed with plates at the ends was encased in an outer iron tube, leaving a space between in which was the bulb of a thermometer. The iron tube could be surrounded by a freezing mixture or placed in a bath, and it served to protect the glass and also to ensure an equable distribution of temperature. A beam of light was passed through the glass tube, which had a layer of liquid occupying about one-fourth of its volume on its lower side. An hour was always allowed to elapse before taking an observation, so that the air was thoroughly saturated at the temperature. The following table embodies the results:—

Percentage composition of mixture. Sulphur.	Bromine.	Formula (about).	Absorption spectrum failed to be visible (about).
56	44	S_5Br	+ 42°
50	50	S_5Br_2	+ 33
44	56	S_2Br	+ 25
35	65	S_4Br_3	+ 13
28·57	71·43	SBr	+ 3
22	78	S_2Br_3	− 7
17	83	SBr_2	visible at − 18

The numbers here given are the average of several experiments, which show a variation of at most two degrees for the disappearing point. A curve might be constructed showing the varying force with which bromine is held by different quantities of sulphur; but as the above table is not absolute, and is sufficient to show that the question is a physical and not a chemical one, a graphic representation would not teach us much.

It was stated in my former paper, that on heating the liquid it began to boil at about 80°, and the thermometer rose without one *continued pause* till the boiling point of sulphur is reached. I find that on

taking a large mass of the mixture, it begins to boil as low as 72°, but it very quickly rises—only a very small distillate containing a very large percentage of bromine (about 96 per cent.) being obtained below 80°. By taking portions boiling between any two temperatures, any compound of sulphur and bromine may be said to have an existence; but although a large portion of the liquid distils over between 190° and 230° (and this contains the calculated boiling points of mixture of SBr and SBr_2), if this portion be redistilled, it will be found to yield no definite compound and to have no fixed boiling point. Thus, a quantity of about 50 c.c. of SBr was placed in a distillation-bulb and heated on the water bath for two days, when it was found that 15 c.c. of a distillate were obtained, having a composition approaching S_3Br_5, containing 20·62 per cent. sulphur and 79·38 per cent. bromine. This was put back and the liquid heated repeatedly up to 120°. It was found that, after cooling each time, the thermometer invariably showed 80° as the primary boiling point, and rose up to 120° just as before; 24·8 c.c., or about one-half of the liquid, came over, after five distillations, having the composition of about S_2Br_3, containing 23·5 sulphur and 76·5 bromine. This was again put back and the liquid made up to SBr, as it had suffered a small loss of bromine. Another series of distillations was undertaken, allowing the temperature to rise to 180°. After the fourth distillation, 34·2 c.c. of liquid were found in the receiver, constituting rather more than two-thirds of the original liquid, and having a composition approaching S_3Br_4, containing 23·8 per cent. of sulphur and 76·2 per cent. of bromine. I do not give the analytical numbers, as none of the analyses I have made agree well with any formulæ, and I am sure no bodies of these formulæ exist, the experiments being detailed to give an idea of the way in which the mixture can be manipulated. In every one of these distillations there was dissociation, as on looking at a source of light through the vapour, the spectroscope showed at any moment the characteristic bands of bromine. Thus, although SBr was supposed to distil at about 200°, two-thirds may be distilled over below 160°, leaving a body containing 39 per cent. of sulphur and 61 per cent. of bromine, or about S_3Br_2. We thus see that, as in ordinary mixtures, the body with the higher boiling point retains that which boils at a lower temperature with increasing tenacity the larger the proportion of the former in the liquid. If we say that it is a case of weak chemical combination, we must admit that no sudden dips occur at the multiple proportion points; that is, that there is an infinite number of compounds arranged along a curve.

Then as to the heat of formation. On mixing 40 c.c. of bromine with the requisite amount of sulphur, the thermometer rose 21°; that is, from 14° to 34°, so that the amount evolved is really inconsiderable.

Mr. Muir indeed stated in a paper published since mine, that a great deal of heat was evolved, but I have Mr. Muir's authority for stating that he was wrong in so stating the case. What he meant to convey was, that a considerable rise of temperature was observed. But still the fact remains that some heat is evolved, and this must be caused either by chemical action or by change of state. That some at least of the heat is due to the latter cause is, I think, shown by the following facts:—When nearly all the bromine is distilled off the mixture, the sulphur left is always viscid and very like plastic sulphur; and on adding the limpid liquid bromine to sulphur, it is not a limpid liquid which is formed, but a body as viscid as oil of vitriol, and not at all like sulphur chloride or a solution of sulphur in carbon disulphide. Now as we know that insoluble sulphur does not combine with bromine, and as the action of the latter on sulphur evidently partakes very much of the action of a solvent, it seems likely that sulphur dissolves, not as octohedral sulphur, but as the plastic variety, and that the heat evolved may be due to the conversion or change of state. A quantity of plastic sulphur was formed, and it was found to be much more readily soluble in bromine than the ordinary variety, and did not evolve so much heat in solution; in equivalent experiments the thermometer rose for ordinary sulphur 20°, and for plastic only 12°. The plastic sulphur is never pure, as there is always left a considerable amount of insoluble sulphur (in one experiment 15 per cent.). The plastic sulphur used was obtained by suddenly cooling fused sulphur in the ordinary way. As the thermal relations of those varieties of sulphur are still matters of dispute, no exact calorimetrical observations were made, but from the above it seems very probable that a portion of the heat evolved by the action of bromine upon sulphur is due to the change from octohedral to plastic sulphur.

Next as to the volumes of the various mixtures. I have given the sp. gr. of SBr in my former paper as 2·629, and five determinations made since at different times and at 4° give 2·629, 2·627, 2·627, 2·628, and 2·629; average, 2·628. It will be seen that as the mean of the sp. gr. of the constituents (S = 2·050, Br = 2·980) is 2·515, the mixture is denser by ·113 than mere mixture would give, showing a contraction of 4·34 per cent. on mixing the constituents. It occurred to me that an examination of the sp. gr. of various mixtures would elucidate the nature of this contraction, and show at what point it was greatest, and whether any multiple proportion-compounds could be discovered. The work was done with an apparatus I have described elsewhere (*Chem. Soc. Journ.*, vol. xii, 1874, p. 203), which, owing to the great ease with which it can be emptied and cleaned, enabled me to do sp. gr. determinations at the rate of six per hour. The following table embodies the result of the work, which for convenience was done

with multiple proportion-mixtures. The column headed "calculated" is what the sp. gr. ought to be if it were a mere mixture:—

Mixture.	Found.	Average.	Calculated.	Difference.
1. S_3Br.	2·295, 2·290, 2·294	2·293	2·282	·011
2. S_2Br.	2·430, 2·420, 2·425	2·425	2·360	·065
3. SBr.	2·627, 2·628, 2·629	2·628	2·520	·108
4. SBr_2.	2·823, 2·820, 2·817	2·820	2·670	·150
5. SBr_3.	2·880, 2·881, 2·879	2·880	2·749	·129
6. SBr_4.	2·900, 2·910, 2·905	2·905	2·795	·125

It is plain from these numbers that the sp. gr. increases rapidly with the bromine up to the compound SBr_2, and this is brought out more clearly if we consider that the sulphur only is affected in volume, and that the bromine is constant. On such a supposition, the sp. gr. of the sulphur in the above mixture would be:—

Pure Sulphur	2·050
No. 1	2·065
„ 2	2·147
„ 3	2·266
„ 4	2·590
„ 5	2·570
„ 6	2·600

This plainly shows that up to No. 4 each increment of bromine doubles the increment in sp. gr., but beyond that we have very little effect. At SBr (or S_2Br_2 supposed) we have no sudden change, so that, pyknometrically, it has no existence. It is my intention to measure the amount of heat evolved on making the above mixtures, to find if, as would be expected, it is proportioned to the contraction. Thus we find that the effect of bromine upon sulphur increases till it has formed the same body as it does with chlorine, and that, as with chlorine, it has a feeble effect above SBr_2. If, however, we go upon the supposition that all compounds below SBr_2 are mixtures of that

body with sulphur, we find that this does not hold. Let us take the case of $S_2Br.2S_2Br = SBr_2 + 3S$, which would give $(2{\cdot}050 \times 3 + 2{\cdot}820 \div 4 = 2{\cdot}285$, and we find the actual number to be 2·425, and so with any other of the series we find the observed sp. gr. higher than that calculated on the assumption of the existence of SBr_2. From this we see that *the action of any quantity of bromine upon any quantity of sulphur is an action on the whole mass, and not in multiple proportion.* Thus we find that the action of bromine upon sulphur is on the borderland between solution and chemical combination, the general action being that of a solvent, and the greatest contraction being at SBr_2, pointing to multiple proportion action.

Since the proportion SBr_2 seemed to give the maximum of action, it was thought that an examination of the freezing points of various mixtures might throw some light on relations between them, but it was found that, except when the proportion of bromine was very large, the mixtures would not freeze, but became thick like tar. It seems strange that mixtures of bromine and sulphur should remain liquid below the temperature at which bromine freezes, yet this is the case: in fact SBr is quite liquid when bromine is solid. At temperatures approaching −30° the mixture only becomes more viscid. No information can be got in this way, except a confirmation of the changed state of the sulphur and of the *general* action of the bromine, as no multiple proportion hereby crystallises out. As shown further on, however, when other bodies are present capable of forming molecular compounds with SBr_2, the two crystallise together, thus affording evidence of a certain amount of chemical action. Since the temperature of boiling varied constantly, that is to say, the liquid always gave off portions of vapour containing more bromine than the residue, it appeared to be desirable to measure the vapour-tension at temperatures below the boiling point to find if it became constant for successive portions at temperatures where the vapour over the liquid did not show the absorption-spectrum of bromine. The "time method" which has been described in this Journal* was used, and the following experiments made. First an examination of the mixture SBr at the ordinary temperature of the laboratory (16°) was made. The following table embodies the results:—

* Examination of substances by the time method (*Chem. Soc. Journ.*, 1877, No. II, page 381).

Hours.	Pure air passed (litres).	Weight carried over.
1	·5	·0285
2	,,	·0282
3	,,	·0280
4	,,	·0275
5	,,	·0271
6	,,	·0263
7	,,	·0254
8	,,	·0246
9	,,	·0230
10	,,	·0218
11	,,	·0203
12	·4	·0175

Five grams of liquid were employed, and the total loss was ·2985, and the increase in the weighing tube was ·2982. On analysis the portion carried over had the composition 78·07 per cent. Br and 22·04 S, agreeing accidentally with the formula S_2Br_3, which requires 78·94 Br and 21·06 S. I say accidentally, for it is evident that as the vapour-tension was decreasing; had the time been lengthened, a formula higher in sulphur would have been obtained. On subtracting the bromine and sulphur from the original amount used, there is left a liquid in which the sulphur and bromine have the ratio S 427, Br 417. So that here again we see that an indefinite mixture is obtained and not a multiple proportion body. On passing air over the mixture at 0° for two days the specific gravity was reduced from 2·628 to 2·614, and in another three days to 2·604. The action was allowed to go on for four days longer, when it was found that the density was 2·571, which is much below SBr, and would agree roughly with a mixture of about S_3Br. Thus, even at 0°, there is no fixed composition.

In the paper before referred to I stated that when metallic arsenic is added to the mixture of sulphur and bromine (SBr) heat was evolved and a red liquid formed which contained a new compound. When sufficient arsenic is added to the liquid, arsenic bromide is formed, and even arsenic sulphide; but if the quantity be small and the liquid subsequently cooled to —18°, beautiful dark-red crystals of the new compound are obtained which may be separated from the excess of liquid compounds, and then melted and again crystallised and drained. They were found to melt at about —17° and form a red liquid containing arsenic, sulphur, and bromine. The liquid had the sp. gr. of 2·789, and was decomposed by water into arsenious acid, hydrobromic acid, and sulphur. On analysis it gave a composition equal to a body with a formula AsS_2Br_3 as shown by the following analyses:—

	Found.			Calculated.
As.....	20·43	20·07	18·52	19·79
S	16·00	16·23	17·04	16·88
Br.....	63·51	64·24	63·70	63·33
	99·94	100·54	99·26	100·00

This body, which is evidently a multiple proportion compound, is most likely a compound of arsenic sulphobromide and sulphur dibromide after the following formula, $AsSBr.SBr_2$. The only other simple formula which would fit the above analyses is $AsBr_3.S_2$, which would mean, I think, a mechanical mixture, and this is not the case. I think that the evidence I have already adduced for the existence of SBr_2 renders it probable that when at low temperatures it meets a body with which it can form a molecular combination, it assumes the crystalline form in conjunction with such a body. In conclusion, my whole work seems to show that the action of bromine upon sulphur increases in a regular manner up to SBr_2, totally ignoring the point SBr, and that above SBr_2 we may have another curve to SBr_4, and then another fainter echo to SBr_8, and so on; but of the existence of S_2Br_2 we have at present no evidence.

XXXIV.—*On Essential Oil of Sage.*

By S. Sigiura, Student in the Laboratory of The Owens College, and M. M. Pattison Muir, Prælector in Chemistry, Caius College, Cambridge.

1. In a paper published in the *Philosophical Magazine* for November, 1877, are embodied the results of our experiments upon essential oil of sage so far as these results had then extended. We have continued the inquiry since that date, and are now desirous of laying our further results before the Society. We are aware that these results are incomplete, but, inasmuch as we do not propose continuing the investigation together, we think it desirable that a communication should be made of the results which we have conjointly obtained. One of us will continue the examination of the constituents of sage oil, and hopes on a future occasion to lay the results before the Society.

2. We were supplied by Messrs. Wright, Layman, and Umney with a quantity of sage oil recently distilled at Leipzig. The oil was of a yellowish-green colour; it had a powerful odour of sage and a burning

taste. When it was submitted to distillation, a little water came over, after which the temperature rose rapidly to 180°, at which point a colourless oil began to collect in the receiver. The greater portion of the oil came over between 180° and 220°, a thick resinous black liquid remaining in the flask.

The main portion of the oil boiled between 180° and 205°. After repeated fractionation over sodium of the portion boiling below 180° it was split up into two main quantities, upon both of which sodium was without further action.

3. The first, and much the smaller, quantity boiled at 152—156°; it had a specific gravity of 0·8435 at 15°; its refractive index at 20° for line D was 1·4607: 100 millimeters rotated the polarised ray 10° 38′ to the *right*.

For the determinations of the action of the polarised ray upon the various bodies mentioned in this paper we are indebted to Dr. Tilden. We beg most heartily to thank him for his kindness.

The following numbers were obtained on analysis:—

0·301 gram gave 0·975 gram CO_2 and 0·31 gram H_2O.

	Calculated for $C_{10}H_{16}$.	Found.
Carbon	= 88·23	88·36
Hydrogen.....	= 11·77	11·44

This terpene appeared to contain small traces of cymene, as shown by treatment with strong sulphuric acid in the usual way.

4. The second and larger portion, obtained by fractionating the oil which boiled below 180° over sodium, boiled at 162—167°: it had a faint smell of turpentine: a specific gravity of 0·8653 at 15°; a refractive index at 20° for the line D of 1·4658; and a 100 millimeter column rotated the polarised ray 11° 34′ to the *right*.

0·250 gram gave 0·8125 gram CO_2 and 0·255 gram H_2O.

	Calculated for $C_{10}H_{16}$.	Found.
Carbon	= 88·23	88·64
Hydrogen.....	= 11·77	11·33

This terpene also contained a small quantity of cymene.

5. About 10 grams of the terpene, boiling at 162—167°, was heated with a large excess of dilute chromic liquor. During oxidation much carbon dioxide was evolved, and the oil gradually became thick. The unattacked oil, after 37 hours, amounted only to a few drops. A small quantity of terephthalic acid was produced, doubtless by oxidation of the cymene present.

After distilling the green liquid, neutralising with caustic soda, concentrating, and distilling with sulphuric acid, an acid liquid was ob-

tained which yielded a silver salt giving the followiug numbers on analysis :—

0·0525 gram gave 0·0335 gram silver.

	Calculated for C_2H_3OOAg.	Found.
Silver	= 64·67	63·90

6. About 15 grams of the 162—167° terpene was heated with about eight times its own bulk of diluted nitric acid (1 : 1). After red fumes had ceased to be evolved, a small quantity of a resinous material was noticed, but the quantity was too small for examination. The liquid was neutralised with barium carbonate, and the precipitate so produced was decomposed by sulphuric acid; on filtering and evaporating crystals were obtained, which, on conversion into a calcium salt, gave the following analytical numbers :—

0·094 gram gave 0·0635 gram $CaCO_3$.

	Calculated for $CaC_2O_4H_2O$.	Found.
Calcium	= 27·40	27·02

No acid other than oxalic was found in the product of the action of nitric acid upon this terpene.

7. On treatment with bromine at a low temperature and subsequent distillation, a liquid, smelling like cymene, boiling at 175—179°, and having the specific gravity of 0·869 at 14°, was obtained.

On combustion this liquid gave the following numbers :—

0·292 gram gave 0·950 gram CO_2, and 0·282 gram H_2O.

	Calculated for $C_{10}H_{14}$.	Found.
Carbon	= 89·55	88·72
Hydrogen.....	= 10·45	10·72

The reaction, $C_{10}H_{16}Br_2 = C_{10}H_{14} + 2HBr$, had, therefore, most probably taken place: the whole of the terpene was not, however, converted into cymene, a considerable portion being resinised.

8. Neither gaseous hydrochloric acid nor an aqueous solution of the gas gave any solid compound with the 162° terpene: on distilling the oil saturated with the acid it evolved a large quantity of hydrochloric acid, and distilled almost exactly at the same temperature as the original oil.

9. These results show that the two terpenes obtained from the sample of sage oil upon which our latest experiments have been carried out differ in many points from the terpenes having similar boiling points obtained from the sample of oil with which we formerly worked. The main points of difference are in specific gravity, refractive indices,

and, chiefly, action on the polarised ray. We note these points in tabular form.

			Sp. gravity at 15°.	Sp. refract. energy.	Sp. rotatory power.
Former terpene boiling at		157°	0·8635	0·534*	− 37·3
Present	,, ,,	152°—157°	0·8435	0·546†	+ 12·4
Former	,, ,,	167°	0·8866	0·522*	− 19·9
Present	,, ,,	162°—167°	0·8653	0·538†	+ 13·4

The respective ages of the samples of oil may throw some light on these discrepancies, but can scarcely, we think, entirely explain them.

We have reason to believe that the later sample is really genuine, but Messrs. Wright cannot give us a guarantee of this. The same firm has distilled for us a quantity of sage, obtaining from about 600 lbs. of the plant about 6 oz. of oil. The results (so far as they have extended) of the examination of this absolutely pure oil will be detailed in the sequel. Most unfortunately the quantity of terpene boiling near 165° obtained from pure sage oil was too small to admit of determining its optical properties.‡

10. On fractionating that portion of the original oil which boiled between 180° and 215°, the greater portion was obtained as a colourless heavy oil boiling from 197° to 203°. This liquid was undoubtedly salviol (see *Phil. Mag.*, November, 1877).

11. Salviol has a specific gravity of 0·934 at 15°, and a refractive index for the D line at 20° of 1·4623: hence specific refractive energy = 0·495: a column 100 millimeters in length rotates the polarised ray 15·13° to the *right*: hence specific rotatory power = +16·19.

12. About 12 grams of salviol was heated with eight times its bulk of diluted nitric acid (1 : 1) in a flask fitted with an upright condenser, until red fumes ceased to be evolved. A crystalline substance was then found inside the condenser. A heavy dark-coloured oil formed and sunk to the bottom of the flask: on separation and distillation with water this oil yielded crystals resembling those found in the condenser. The crystalline body melted at 174°, smelt like common camphor, and gave the following numbers on analysis:—

0·158 gram gave 0·4545 gram CO_2 and 0·151 gram H_2O.

	Calculated for $C_{10}H_{16}O$.	Found.
Carbon	78·94	78·45
Hydrogen	10·53	10·67

The acid liquid on cooling deposited crystals which were found to consist of oxalic acid.

* For line A. † For line D.

‡ I hope to have a further quantity of the pure oil distilled for me, and to examine the lower-boiling terpene optically.—M.M.P.M.

0·325 gram of the calcium salt gave 0·220 gram $CaCO_3$ = 27·07 per cent. of calcium.

The gaseous products evolved during the oxidation were led into caustic soda solution, which was afterwards found to contain a large amount of cyanide, besides carbonate, of sodium.

A similar reaction was obtained by oxidising salviol with chromic liquor; a very small quantity of a camphor-like body was produced. In the most favourable experiment about 1 per cent. of the salviol was converted into camphor.

13. No definite compound was obtained by the action of a saturated aqueous solution of hydrochloric acid upon salviol. When the two liquids were heated to 100° in a sealed tube, an oil was obtained which gave off hydrochloric acid when distilled, boiled after one or two distillations at 185—190°, and had a specific gravity of 0·933 at 15°. From an alcoholic solution of this oil, an alcoholic solution of silver nitrate precipitated chlorine as silver chloride; the amount of chlorine thus obtained amounted only to 3·5 per cent.

14. On treating salviol with bromine, a dark red liquid was obtained, which evolved much hydrobromic acid on distillation and boiled chiefly from 180° to 195°. When this liquid was washed with caustic soda solution it darkened much in colour, and, on standing, became more viscid, and deposited a camphor-like solid melting at 173—175° after sublimation, and giving numbers for carbon and hydrogen in the proportion required by those for the formula of camphor. The liquid was not completely decolorised by washing with soda: it continued to evolve hydrobromic acid on distillation.

15. About 12 grams of salviol was distilled with a large excess of phosphorus pentoxide; distillation began at about 170°, the greater portion of the distillate came over between that point and 190°. After repeated redistillations over the pentoxide, the greater portion of the oil, excepting that which was resinised, boiled between 179° and 181°. This liquid had an unpronounced smell of cymene.

(1.) 0·245 gram gave 0·799 gram CO_2 and 0·238 gram H_2O.
(2.) 0·3415 „ „ 1·110 „ „ 0·3395 „ „

	Calculated for		Found.		
	$C_{10}H_{14}$.	$C_{10}H_{16}$.	I.	II.	Mean.
Carbon	89·55	88·23	88·93	88·63	88·78
Hydrogen ..	10·43	11·77	10·79	11·04	10·92

The liquid is evidently cymene, containing probably a small amount of terpene. On treating a portion of the liquid with sulphuric acid it was partially resinised; the non-attacked portion had a marked odour of cymene.

16. A quantity of salviol was heated to 130° in a sealed tube for two or three days, the salviol had then changed in colour and smell, and boiled above 210°; no solid body was formed.

These experiments, we think, confirm our former formula for salviol, viz., $C_{10}H_{16}O$. We cannot as yet give an explanation of the production of camphor from salviol; this subject, and, indeed, the whole question of the relations of the oxidised to the non-oxidised constituents of sage oil is reserved for a future communication.

17. Our present sample of sage oil yielded but a very small amount of camphor; the amount of camphor is very evidently dependent upon the age of the oil.

18. Messrs. Wright, Layman, and Umney distilled for us about 600 lbs. of sage, obtaining 6 oz. of oil. One portion of this oil (amounting to $4\frac{3}{4}$ oz.) was distilled during the summer of 1877, the colour was reddish-brown, with but a very faint shade of green; the remainder, distilled during the winter of 1876–77, was possessed of a distinct green colour. The reaction of both samples was neutral, the taste and smell similar to those of the commercial oil.

After drying by contact with fused potassium carbonate, the oil (both quantities mixed) had a specific gravity of 0·9258 at 17°.*

19. Distillation began at about 210°, the greater portion passing over between 260° and 265°. A small quantity distilled above 310°, and was possessed of a bluish colour, which changed to brown on standing in light. The colours of all the fractions darkened very considerably on standing in diffused sunlight for a few days.

A thick, semi-solid, tar-like mass, amounting to about 6 per cent. of the total oil, remained non-volatile below 310°.

The various fractions had but a slightly pronounced odour of sage; those of higher boiling points possessed the smell of tar.

After repeated fractionations over sodium, about 5 per cent. of the total oil was obtained as a colourless liquid, smelling of sage, and boiling from 166° to 171°. A very small quantity boiled between 240° and 250°, but the boiling point of the main portion was situated at 264° to 270°. Very small portions boiling at 270—290° and 290—310° respectively were obtained; the colour of these, especially of the latter, was greenish-blue.

No camphor was obtained by distillation, nor by pressing the resinous mass which remained after distillation.

20. The fraction boiling at 166—171° was too small to admit of much being done with it; the specific gravity of this oil (terpene ?) was 0·8667 at 15°.

21. The fraction boiling at 264—271°, which constituted about

* It was afterwards shown that this oil contained traces of water.

three-fourths of the total oil, was of a dark emerald-green colour, of a somewhat viscid nature, and had but little smell of sage.

0·205 gram gave 0·663 gram CO_2, and 0·211 gram H_2O.

	Calculated for $C_{15}H_{24}$.	Found.
Carbon	88·23	88·20
Hydrogen	11·77	11·42

The following are the results of specific gravity determinations:—

Specific gravity at			
0°.	12°.	24°.	41°.
0·9198	0·9137	0·9072	0·8970

A column 100 milimeters in length rotated the polarised ray 3° 14′ to the *right*.*

This terpene was only very slightly soluble in alcohol; it was rapidly darkened and almost completely resinised by strong sulphuric acid, even when surrounded with a freezing mixture. Bromine converted the terpene into a dark viscid mass, which could not be distilled. Sodium was without action on this terpene. On oxidation with chromic liquor, acetic and carbonic acids were obtained, as also a small quantity of a semi-resinous body, which could not be purified. No stable hydrochloride was produced by the action of gaseous hydrochloric acid on the cooled terpene.

XXXV.—*On the Detection and Estimation of Free Mineral Acids in various Commercial Products.*

By Peter Spence, F.C.S., and A. Esilman, Manchester.

The determination of free mineral acids under ordinary circumstances is a very simple matter when we are provided with a standard alkaline solution, and a few drops of litmus; but the increasing requirements of chemical industries render it imperative upon the chemist to discover and estimate with exactness these acids *in the presence of salts having an acid reaction, or it may be of other acids.* All persalts, and salts of zinc, copper, &c., it is well known, distinctly redden litmus paper,

* This number is approximate only: it was obtained by calculation from a shorter column.

although they may be basic in constitution, and standard alkali fails to distinguish sulphuric from acetic acid.

Of late years, the manufacture of sulphate of alumina from china clay and bauxite has assumed great importance, arising from the immense quantities used in paper-making, and as it is not a product capable of purification by crystallisation like alum, the quality of the article is in too great a degree dependent on the skill and conscientiousness of the manufacturer. The paper-maker is often too little of a chemist to decide which of several samples is the best, when, as is almost invariably the case, the whitest to the eye and strongest to the taste contains the most free acid and least alumina.

Our method is based on the fact that peracetate of iron, even in dilute solutions, has a distinct yellow colour, not perceptibly altered by acetic acid or solutions of persulphates, but instantly bleached by free sulphuric, hydrochloric, and nitric acids. The solution is made by dissolving 10 parts of iron alum and 8 parts of crystallised acetate of soda (both previously dried on blotting-paper) in 1,000 parts of acidulated cold water, made by mixing 920 parts of water and 80 parts of distilled acetic acid (25 per cent.).

Any person of ordinary intelligence, when provided with this solution, can in a few minutes readily determine the relative quantity of free acid in a cake by putting a piece about the size of a pea in a small white basin or cup containing two or three drops of cold water. Add one drop of the test-solution and shake. If the colour disappears add another, and so on until a slight yellow tint remains. In proportion to the number of drops bleached will be the acid character of the cake, and if that number be divided by five, the answer will approximately represent the percentage of free acid. For dropping the test-solution into the basin, we have found most suitable a small glass stoppered bottle, the stopper of which has a slit on each side, made by means of a file. This bottle, when inverted, allows the liquor to drop out without removing the stopper, as the air enters the upper slit, while the liquor drops out through the lower. The acetic acid is added to render the otherwise decomposible solution perfectly stable on keeping.

With most cakes in the market, bleaching of more than one drop will be instantaneous.

We have only met with one aluminous salt, excepting crystal alum, that does not affect the solution.

For this test it is not necessary to separate silica, present in most aluminous cakes.

When the material under examination is in the liquid form, a convenient quantity, say 200 grains, or, roughly, $\frac{1}{2}$ oz., is weighed out in a small beaker, and a standard solution of caustic soda run in from a burette, stirring after each addition, until two or three drops put in a

small white porcelain basin do not perfectly bleach one drop of the acetate solution.

Highly coloured mixtures are of course not well adapted for this test, but these do not occur in practice.

For accurate quantitative determinations the best procedure we have found to be as follows:—Dissolve 200 grains of the sample in the acetic acid water previously mentioned, triturating in a small mortar until all the soluble is extracted. Now add from a burette *strong* solution (made by dissolving 10 parts iron-alum and 8 parts of crystallised acetate of soda in about 50 parts of acidulated water) of the peracetate until the mixture has a decided yellow tint, showing that all the free acid has been neutralised. Dilute to 100 measures with the acetic acid water, and filter off a portion into a test-tube. In another test-tube put as many measures of the strong acetate of iron solution as have been used for the cake solution. Dilute to about 80 measures with acetic acid water, and drop in standard solution of sulphuric acid until the colour is the same as in the other test-tube. The bulk of the liquor must be so arranged that it equals that of the other, viz., 100 measures. The amount of sulphuric acid used is the measure of the free acid in the cake, and divided by 2 gives the percentage.

In this way the results are wonderfully concordant and remarkably expeditious, and we may say we have used it daily for the last two years. Even alum, which has always been understood to be a perfectly neutral salt of alumina, can be readily proved by it to contain small, though commercially insignificant, proportions of free acid, when large quantities are recrystallised, and the free acid is thus concentrated in the mother-liquor.

Other applications of this property of peracetate of iron may be suggested, such as the estimation of free acid in salt-cake, furnaced sulphate of potash, sulphate of ammonia, acetic acid, &c.

XXXVI.—*Action of Hypochlorites on Urea.*

By H. J. H. Fenton, B.A., University Laboratory, Cambridge.

E. W. Davy, in 1854, proposed a method of estimating urea, by measuring the volume of nitrogen evolved from it when acted upon by a hypochlorite. His numbers show that he obtained nearly the whole of the nitrogen in this way. The results of subsequent authors are

similar, but do not appear to be always constant. Handfield Jones, for instance, remarks that "every solution of chloride of soda does not answer equally well."

A pupil of mine (Mr. Street) in this laboratory, wishing to estimate urea, happened to use this method, but added an excess of caustic alkali, to ensure, as he thought, the retention of the carbon dioxide formed in the reaction. On calculating his result, we found that only about half the theoretical volume of nitrogen had been obtained.

I have since found that it is invariably the case, that when urea is acted upon by a hypochlorite in the cold, in presence of a caustic alkali, only half the nitrogen is evolved. Thus—

	Urea.	Theory.
·13841 gram gave	25·31 c.c. N (corr.)	— 51·6
„ „	25·49	
„ „	25·59	
·06571 gram gave	11·9 c.c. N	— 24·5
„ „	11·9	
„ „	12·3	
„ „	11·7	
„ „	12·2	
·3291 gram gave	60·76 c.c.	— 122·7

The mean of 18 experiments gave 18·22 per cent. of nitrogen, theory requiring 37·3.

Several samples of hypochlorites were tried, prepared in various ways; also urea from different sources, and all gave the same result.

Afterwards I tried the effect of using an alkaline carbonate in place of caustic alkali, and in this case nearly the whole of the nitrogen was evolved.

Thus with the same sample of hypochlorite, ·10303 gram urea gave 35·3 c.c. N., when only sodium carbonate was present, but 19·02 in the presence of caustic soda. (Theory = 38·4.) This difference probably accounts for the inconsistent results obtained by many authors.

My object was then to find out what becomes of the remaining half of the nitrogen, when caustic alkali is present. It is evident that it cannot remain as urea, for on adding a large excess of either a hypobromite or hypochlorite to the residue, no further evolution of gas takes place. For the same reason it cannot remain as an ammonia salt, hypochlorites and hypobromites evolving approximately the whole of the nitrogen from these. Moreover, the residue gives no reaction with Nessler's solution; but if, after reducing the excess of hypochlorite with sulphurous acid, the solution be acidified with dilute hydrochloric acid, and again rendered alkaline, an abundant reaction

is obtained with Nessler's test, and the liquid, if treated with a hypochlorite or hypobromite, gives the remaining half of the nitrogen.

Thus ·10999 gram urea gave 19·89 c.c. and 19·7 c.c. respectively, in two experiments with hypochlorite. After reducing, acidifying, evaporating to a small bulk, and rendering alkaline with NaHO, the first gave 19·41 c.c. N, with NaClO, and the second 19·29 c.c. with NaBrO. From these results I concluded that the second half of the nitrogen remains as a cyanate, the reaction of a hypochlorite on urea in presence of caustic alkali, being—

$$2N_2H_4CO + 3NaClO + 2NaHO = 2NaCNO + N_2 + 3NaCl + 5H_2O.$$

In order further to confirm the presence of cyanate in the residue, I reduced with sulphurous acid, as before, carefully neutralised with dilute nitric acid, and added excess of silver nitrate. The precipitate so obtained was digested with dilute hydrochloric acid, and this acid solution gave abundant evidence of ammonia with all tests, whereas only traces could be found in the silver nitrate filtrate when treated in the same way.

Cupric nitrate likewise gave a greenish precipitate in the neutral solution after reduction with ferrous sulphate and filtering. It will be seen in the above equation, that no carbon dioxide is formed in this reaction. This was confirmed by acting on urea with a clear solution of calcium hypochlorite, containing excess of lime-water. Half the nitrogen was evolved as usual, and no precipitation took place. If, however, a nearly neutral solution of calcium hypochlorite be used, the solution at first remains clear; but on standing for some time, a further evolution of nitrogen and gradual separation of calcic carbonate take place.

A solution of pure potassium cyanate evolved no trace of gas with either hypochlorite or hypobromite, in presence of a caustic alkali.

This reaction may, perhaps, help to throw light on the constitution of urea; and also, it affords an easy method of detecting and approximately estimating urea in presence of ammonia salts.

For detection, it is only necessary to treat with a hypochlorite and caustic alkali, until all action had ceased, and then test for cyanate as above. For quantitative estimation, the solution is divided into two equal parts, one treated with hypochlorite and caustic alkali, and the other with hypobromite, and the evolved nitrogen measured.

There appears to be a mean loss of about $2\frac{1}{2}$ per cent. of the evolved nitrogen in all hypochlorite reactions, whether from urea or ammonia salts, and of about 8 per cent. in hypobromite reactions, in ordinary forms of apparatus. (The greater loss with hypobromite is probably due to its far more rapid action, and consequently greater chance of spirting, Sleich having shown that by passing the evolved gas

through more hypobromite, the loss is reduced to 1 per cent.) Thus ·10728 gram urea evolved 21·95 c.c. N as a mean of six experiments with NaBrO. (Theory = 24·009.)

·11957 gram NH_4Cl gave 23·14 c.c. N with NaBrO. (Theory = 25·01.)

·060 gram NH_4Cl gave 12·16 c.c. N with NaClO (in presence of caustic soda). (Theory = 12·54) = each as a mean of two experiments.

Thus, if A and B are the volumes of nitrogen (in cubic centimeters) obtained with hypobromite and hypochlorite respectively, and x the weight of urea (in grams)—

$$\left(\frac{A \times 100}{92}\right) - \left(\frac{B \times 100}{97{\cdot}5}\right) = \frac{x \times 373}{2}$$

In order to verify this equation, two mixtures were taken, each containing ·05202 gram urea, and ·02433 gram NH_4Cl. The first treated with NaBrO gave 22·77 c.c. N, and the second with NaClO gave 15·05 c.c. N.

By the above formula this gives x = ·0499.

I tried several forms of apparatus for these experiments, but wishing to perform many operations at the same time, I found the following the most simple and convenient. A small flask is fitted with an india-rubber stopper and delivery tube; the latter just dips under the surface of water in a shallow dish, and when the stopper is adjusted, is quite full of air. The solution to be examined is introduced, and the acting liquid placed in a separate tube inside the flask, as usual. This latter precaution is generally unnecessary in hypochlorite reactions, especially with urea, as the action does not begin for some time.

A graduated gas-tube is now placed over the orifice of the delivery tube, and the action commenced. The flask is shaken from time to time, due precautions being taken to keep the temperature constant from beginning to end of the operation. When the evolution has entirely ceased the delivery tube is still just full of gas, so that the volume collected is a true measure of that evolved. The delivery tube is then transferred to a tall vessel of water, and the volume read off with the usual precautions.

I intend shortly to investigate the action of hypochlorites on other nitrogenous bodies.

XXXVII.—*On the Behaviour of Metallic Solutions with Filter Paper, and on the Detection of Cadmium.*

By Thomas Bayley, Assoc. R.C.Sc.I.

Some time ago, while holding a wet patch, formed by dropping a solution of silver nitrate upon filter paper, in a stream of hydrogen mixed with arseniuretted hydrogen, I noticed that the metal was contained in the centre of the blot, and that the edges for about half a centimeter inwards were entirely free from metal. After being exposed to the gas, the blot presented the appearance of a black spot surrounded by a broad ring of water. I therefore made a few experiments, in order to determine whether filter paper has any power of withdrawing silver salts from solution. 7·8703 grams of silver nitrate having been dissolved in water, and diluted to 500 c.c., a quantity of this solution was placed in a beaker, and a roll of filter-paper, sufficient to absorb nearly the whole, plunged into it. After some minutes the filter-paper was removed, and as much of the liquid as possible squeezed into the beaker. It is clear that the effect of this treatment, unless the paper possesses a power of retaining the salt, would merely be to slightly concentrate the solution by evaporation.

Four experiments were made in this manner, fresh rolls of paper and fresh portions of the standard solution being used in each instance. 25 c.c. of the solution, after treatment with the paper, were mixed with hydrochloric acid, and the precipitated silver chloride dried, ignited, and weighed.

The results were as follows:—

Solution used.	Ag. found.	Ag. originally present.
25 c.c.	·2182 grm.	·2500 grm.
25 c.c.	·2306 „	·2500 „
25 c.c.	·2353 „	·2500 „
50 c.c.	·4760 „	·5000 „

This shows that after a roll of paper has been soaked for a few minutes in a solution of silver nitrate, the quantity of silver has materially diminished. A few experiments made by my friend, Mr. Weston, show that the same is true in the case of mercury salts. Drops of other metallic solutions were placed upon filter-paper, and submitted to the action of sulphuretted hydrogen. I found that in some cases the metal extends to the edge of the spot, and even seems concentrated there, while in others a water-ring surrounds the patch of sulphide.

Further inquiry demonstrated that solutions of the same metal present the first or second of these phenomena, according as they are concentrated or dilute. Taking a strong solution of copper sulphate and diluting portions of it, I found that at one degree of solution the metal spreads outwards just as far as the water, and that with solutions more dilute than this, the water is separated from the metal, which remains in the centre. The more dilute the solution, the broader is the external water-ring. The exact strength of solution to give the former appearance varies with the temperature, and with the kind of paper used; the metal in a warm solution is more mobile than if the solution were cold.

The blot formed by a drop is larger on the whole, but the mobility of the metal is increased in a greater proportion than that of the water. A close Swedish paper is more efficacious in separating the salt than a loose-textured piece of common filter-paper.

A great difference is found to exist among the salts of various metals; the salts of silver, lead, and the persalts of mercury, when moderately concentrated, give a wide water-ring, while the salts of copper, nickel, and cobalt must be much more dilute to present the same appearance. Cadmium seems especially able to pass through filter-paper.

A solution of copper sulphate containing ·001 gram of copper per c.c. was found to give a water-ring; at the same temperature and with the same piece of Swedish paper, a solution of cadmium sulphate of less than half that strength, gave a blot, in which the cadmium extended perfectly to the edge. Metals appear to act in this respect as though other metals were absent; this property of cadmium, therefore, affords an elegant means of detecting it in the presence of metals, the sulphides of which are black.

The considerably dilute solution is dropped upon filter-paper, and the blot allowed to extend as far as possible (this should be done in all cases) and the sulphuretted hydrogen then turned on. The black patch is found to be surrounded by a vivid yellow ring of cadmium sulphide. A solution rich in nickel, cobalt, or iron may in like manner be examined for these metals, in presence of smaller quantities of copper, lead, mercury, and silver.

The blot having spread, is exposed to sulphuretted hydrogen, and afterwards held over a bottle of ammonium sulphide, when the water-ring becomes black. This method, however, is extremely suited to the detection of cadmium. It was found that the presence of free acid much increases the mobility of copper, so that before testing for cadmium in this manner, the solution, if acid, should be made slightly alkaline by ammonia.

Similar experiments with the hydrates of calcium, sodium, and

ammonium dropped upon turmeric paper, showed that the water-ring is formed if the solutions are dilute.

When they are concentrated the alkali extends to the edge of the blot, and indeed seems concentrated there, for the brown patch is surrounded by a ring darker in colour than the other parts.

These properties of metallic solutions are probably closely connected with capillarity.

This investigation was conducted in the Chemical Laboratory of the Royal College of Science, Dublin.

XXXVIII.—*Analogies between the Action of the Copper-Zinc Couple and of Occluded and Nascent Hydrogen.*

By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe, Lecturer on Chemistry in Dulwich College.

We have recently pointed out (this volume, page 139) that finely divided copper charged with hydrogen converts nitre into potassium nitrite and ammonia. Hydrogen in association with the same metal, we have since found, reduces potassium chlorate to the chloride. These results are in perfect agreement with those obtained by the action of the copper-zinc couple on solutions of the same salts.

On thinking further of this matter, it appeared to us that if copper-hydrogen was capable of effecting such a reduction, the platinum or palladium combinations, in which occluded hydrogen enters in much larger quantity, ought to do it with still greater facility. It also appeared desirable to study the action of the copper-zinc couple on other compounds side by side with that of occluded hydrogen, and especially to ascertain whether a metal is absolutely necessary, or whether hydrogen occluded by carbon would act in the same manner.

Our attention was also naturally drawn to that condition of hydrogen which is usually denominated nascent, and to which special power is attributed. It became interesting, therefore, to see whether the reactions usually attributed to nascent hydrogen, such as the reduction of nitrobenzene, of ferricyanide of potassium, of sulphurous acid, of arsenious acid, and of blue indigo, could not be effected under circumstances in which the hydrogen was no longer nascent.

Copper-Zinc Couple.

We find that beside the many reductions previously described, our copper-zinc couple, in presence of water, converts nitrobenzene into

aniline, a reaction which may be utilised for the detection of small quantities of the former substance;* liberates sulphur from sulphurous acid, without, however, producing sulphuretted hydrogen; and converts blue into white indigo in presence of weak alkali.

Palladium-Hydrogen.

A quantity of palladium black was precipitated by the action of an alkaline formate on palladium nitrate, and after washing with water and drying at 100°, it was heated at the same temperature for about 30 minutes, in a current of dry hydrogen, and afterwards slowly cooled in the same gas.

Potassium Nitrate.—An experiment by Böttger showed that nitrite was produced by the action of palladium-hydrogen on this salt. We find that both nitrite and ammonia are quickly produced, but no hyponitrite. A quantitative trial gave the following results, when 100 c.c. of a 5 per cent. solution of nitre were poured at the ordinary temperature on 30 grams of the palladium-hydrogen. Almost immediately after adding the solution, it was noticed to be sensibly warm. The temperature was kept from rising by immersing the flask in water (18°) for 10 minutes.

Time.	Temp.	Quantities in grams.		Hydrogen required by the KNO_2 and NH_3 in grams.	KNO_3 decomposed.
		KNO_2.	NH_3.		
10 minutes.	19° C.	·154	·0094	·0081	·239
30 „	24°	·363	·0375	·0262	·657
60 „	32°	·276	·092	·049	·876
90 „	34°	·191	·143	·072	1·07
120 „	33°	·115	·204	·099	1·35
22 hours.	19°	Nil	·222	·107	1·351

The general result here is the same as with the couple:—no production of hyponitrite, but ammonia and nitrite at the beginning of the action, and the subsequent simultaneous decomposition of potassium nitrate and nitrite.

* Add some twelve drops of strong copper sulphate solution to three or four pieces of zinc foil (1 inch × ½) in about 5 c.c. of water; wait till the liquid is nearly or completely decolorised; pour off the zinc sulphate solution; and wash the conjoined metals three or four times with water. Now add to this couple the nitrobenzene in solution or in suspension in water; heat nearly to boiling for about two minutes; filter if necessary; cool; and add, drop by drop, a solution of bleaching powder. In this way the violet coloration indicative of aniline may be most distinctly obtained in 5 c.c. of an aqueous solution of nitrobenzene containing ·5 gram in 1000 c.c. of water.

Potassium Chlorate.—The couple reduces this salt to chloride without producing any of the intermediate oxy-compounds. The same result is brought about by palladium-hydrogen. We subjoin the results of an experiment for which 30 grams of the hydrogenised metal, and 100 c.c. of a 5·6 per cent. solution of potassium chlorate were employed. The temperature of the solution, on mixing, rose more rapidly than in the corresponding nitre experiment. The flask was immersed in water for 10 minutes.

Time.	Temp.	KCl produced in grams.	Hydrogen required.
10 minutes.	19° C.	0·751	·0605
30 „	33°	1·258	·1013
60 „	29°	1·429	·1152
90 „	27°	1·501	·1209
120 „	—	1·528	·123
22 hours.	—	1·672	·1347

The amount of hydrogen used up in this experiment is some seven times greater for the first 10 minutes than that oxidised by the equivalent nitre solution in the same time. The couple also reduces the chlorate more rapidly than it does the nitrate.

30 grams of the same preparation of palladium-black hydrogenised were heated to redness, when 0·130 gram of hydrogen was liberated. Thus it would appear that the solution of a reducible oxy-salt can extract practically the whole of the hydrogen stored up by the metal, or at least all that can be driven off at a red heat at the ordinary pressure.

Like the copper-zinc couple, palladium-hydrogen is incapable of reducing the potassium perchlorate; but it easily reduces nitrobenzene in aqueous alcohol to aniline; changes blue to white indigo in presence of weak potash-solution; converts solution of sulphurous acid into sulphuretted hydrogen; and reduces a solution of arsenious acid to metal, without, however, the production of arsenuretted hydrogen.

Platinum-Hydrogen.

Some platinum-black was prepared by the method employed for the preparation of the palladium. After precipitation the metal was boiled with a solution of potash until free from ammonia; then, after thorough washing with water, treated with hydrochloric acid, washed until free from acid, dried at 100°, and hydrogenised in like manner to the palladium.

Potassium Chlorate.—120 c.c. of a 5 per cent. solution of this salt were added to 25 grams of the prepared metal. Immediately chlorate

was reduced, corresponding to ·0165 gram of chloride; in 6 minutes, to ·0472 gram; and in 18 hours (when, and probably long prior to which, the action was over), to ·0719 gram.

Potassium Nitrate.—Our experience here is somewhat curious. Some solution was found to be free from ammonia after being in contact with the conjoint elements for some hours. In another trial ammonia was detected in quantity soon after putting the substances together, but in a few hours the solution gave but a very slight coloration with the Nessler reagent.

A quantitative experiment, employing 30 grams of the hydrogenised metal, and 100 c.c. of a 5 per cent. solution of nitre, gave :—

Immediately.....	·006	per cent. ammonia.
2 minutes	·0075	„ „
7 „	·0030	„ „
37 „	·00035	„ „
2 hours	trace of ammonia.	

Another similar experiment, but with a different specimen of the platinum-hydrogen, gave :—

Immediately.....	·0032	per cent. ammonia.
10 minutes	·002	„ „
37 „	·0014	„ „
20 hours	·0004	„ „

Nitrite could not be detected in any of the stages of either of these experiments.

But why does the ammonia pass from solution? The metal being hydrogenised precludes the possibility of the presence of oxygen, which might under the circumstances get rid of the ammonia by oxidation. Is it absorbed by the finely divided metal? The platinum of the first experiment was washed with water, until the washings were free from anything but a mere trace of ammonia, then boiled with hydrochloric acid. Some metal dissolved, owing, perhaps, to adhering nitrate, and the solution, after the removal of this by potash, gave a copious precipitate with the Nessler reagent. The metal of the second experiment was likewise thoroughly washed, then boiled with caustic potash, which set free ·0017 gram of ammonia. The quantity of this substance, taken out in the portions of liquid used for the estimations, amounted to ·0012, which, added to that evolved from the metal by potash, approaches the ·0032 gram found immediately after pouring on the solution. Platinum then abstracts ammonia from solution, which fully accounts for its disappearance in the reaction.

It would appear from these results, that hydrogen associated with platinum is much more energetic than when it is associated with

palladium, although the latter metal fixes a much greater quantity of the gas. This is seen in the amounts of chlorate reduced in the time experiments by the platinum-hydrogen and the palladium-hydrogen respectively. Thus the hydrogen of the palladium-hydrogen reduced in 10 minutes 45 per cent. of the possible quantity, whereas the hydrogen of the platinum-hydrogen reduced in 4 minutes 65·6 per cent. Again, the fact that platinum-hydrogen apparently reduces by one operation the nitrate to ammonia, points to the same conclusion, although there can be but little doubt that this change takes place through the nitrite—in fact, distinct though slight evidence of this was noticed with another preparation of platinum-hydrogen.

In addition we find that platinum-hydrogen readily reduces ferrito ferro-cyanide, and like palladium-hydrogen converts a solution of arsenious acid to metallic arsenic, without the production of arsenuretted hydrogen. With nitrobenzene, however, it produces, not aniline, but a substance which dissolves in alcohol to a red solution, probably azobenzene, and although it reduces a solution of sulphurous acid, it gives no sulphuretted hydrogen.

Carbon-Hydrogen.

Hunter has shown that cocoa-nut charcoal is more absorptive for gases than other kinds of vegetable charcoal. We therefore selected it for our experiments. The first quantitative trial was made by pouring 100 c.c. of a 5 per cent. solution of potassic chlorate on 40 grams of the powdered carbon, hydrogenised by heating to redness and subsequent cooling in a current of hydrogen. Corresponding volumes of solution of potassium chlorate and of water respectively were poured at the same time on similar quantities of the untreated charcoal. In each case the materials remained together for 20 hours at the ordinary temperature (about 18°), when the chloride was estimated by precipitation with silver nitrate, after acidifying with nitric acid. The silver chloride obtained would correspond with 4·2 milligrams of hydrogen for the hydrogenised; 3·2 for the non-hydrogenised with solution of potassium chlorate; and 2·4 for the non-hydrogenised and water. The chloride found in the experiment with water alone represents of course the amount extracted from the charcoal; deducting this from that found in the first experiment, it is seen that the hydrogenised carbon exerts an appreciable reducing action on the chlorate. The difference noticeable between the non-hydrogenised carbon with chlorate and that with water alone may possibly result from the presence of occluded carbonic oxide. In the hope of removing this source of error, and also the chloride and any conceivable traces of iron or carbide, which would doubtless form reducing couples with the

carbon, we digested the powdered charcoal for 20 hours at the ordinary temperature, with a considerable quantity of nitric acid of about 30 per cent. The substances were then heated together to about 50°, after which the carbon was washed with hot water until the washings were free from chloride and acid, and finally dried at about 200°.

40 grams of this carbon were hydrogenised as described, and poured into a flask containing 100 c.c. of potassium chlorate solution at about 0°, the object of the lower temperature being to give the hydrogen greater time in which to act, as we had noticed that, at the ordinary temperature the liquid physically replaces the gas somewhat quickly. The materials remained together for about an hour at 0°, and for some hours at the ordinary temperature. A similar experiment was made with the purified charcoal non-hydrogenised. The silver chloride obtained for the hydrogenised corresponded to 23 milligrams of hydrogen, and only 0·3 for the non-hydrogenised.

Common wood charcoal purified with nitric acid, as described, gave for 40 grams of carbon-hydrogen, chloride corresponding with 2·5 milligrams of hydrogen, whilst a similar quantity of non-hydrogenised gave but the merest trace.

Further proof of this reduction being occasioned by occluded hydrogen is furnished by the fact that carbon-hydrogen loses some of this power on exposure to the air, resembling in this respect platinum-hydrogen and palladium-hydrogen. In an experiment employing 40 grams of hydrogenised carbon of the same specimen as that used in the first of these last two experiments, which had been warmed and cooled in air previously to being put in contact with the chlorate solution, chloride was obtained corresponding with only ·6 of a milligram of hydrogen, from which it appears that the air removed by oxidation about a fourth of the active agent.

Carbon-hydrogen has no action on a solution of nitre, but easily reduces a solution of ferri- to ferro-cyanide of potassium.

Conclusions.

It is evident from these experiments that there is a close analogy between some actions of the copper-zinc couple, of occluded hydrogen, and of the so-called nascent hydrogen.

As to the copper-zinc couple, we conceive that these fresh experiments very strongly corroborate the view which we thought probable in our last paper, that its great power of reduction and hydrogenisation depends on the absorption of hydrogen by the finely divided metal.

As to the hydrogen occluded in metals, it is well known that this does not form any very strongly marked chemical compounds. It is

true that Graham looked upon the palladium combination as an alloy of hydrogen, and Favre, from his thermometric observations, came to the conclusion that it was a definite chemical compound; but other observers have drawn opposite deductions, and our experiments clearly show a close analogy between the chemical reactions of palladium-hydrogen and the combinations of hydrogen with platinum and copper, and even with carbon.

It must, however, be borne in mind that our experiments, while they show a close similarity between the action of hydrogen as occluded by the several elements, show also certain differences, as set out in the annexed table.

Substances employed.	Substances produced by				
	Copper-zinc couple.	Palladium-hydrogen.	Platinum-hydrogen.	Copper-hydrogen.	Carbon-hydrogen.
$KClO_3$, aqueous solution	Chloride*	Chloride	Chloride	Chloride	Chloride
KNO_3, aqueous solution	Nitrite and ammonia*	Nitrite† and ammonia	Nitrite (?) and ammonia	Nitrite and ammonia	Nil.
K_3Cy_6Fe, aqueous solution	Ferrocyanide	Ferrocyanide‡	Ferrocyanide	—	Ferrocyanide
$C_6H_5NO_2$, aqueous or alcoholic solution	Aniline	Aniline	Azobenzene	—	—
Indigo, with weak solution of potash	White indigo	White indigo	—	—	—
H_2SO_3, aqueous solution	Sulphur	Sulphuretted hydrogen	Sulphur (probably)	—	—
As_2O_3, aqueous solution	Arsenuretted hydrogen	Metallic arsenic	Metallic arsenic	—	—

At least three views may be taken of these reactions—

1. That the energy of the hydrogen is increased by its association with a more negative element. This explanation will apply to the carbon combination as well as the others, for the specimens of cocoa-nut and ordinary wood charcoal were found to conduct electricity freely. Upon this view we should expect that the power of these combinations would increase with the electro-negative character of the

* Thorpe. † Böttger. ‡ Graham.

element with which the hydrogen is associated. This seems scarcely borne out by our results, but there are many points that require consideration before this can be fully decided.

2. That the atomic condition of occluded hydrogen differs from that of ordinary hydrogen, the variations shown in the experiments being ascribable to different atomic aggregation.

3. That the increased power of the hydrogen is due to its condensed condition, while the observed differences between the actions of the different combinations result from variations in this respect, and perhaps also from the more or less firm hold which the metal has upon the gas.

The above chemical changes are effected more or less perfectly by nascent hydrogen. But this hydrogen in every case is set free in contact with, or in very close proximity to a metal, which in virtue of the power known to be possessed by such solids very probably condenses and fixes some of this gas. It may therefore be conceived that the activity of the hydrogen under these circumstances is but the consequence of its intimate association with the metals, or, in other words, of its being in the occluded condition.

XXXIX.—*The Temperatures at which some of the Alkaloïds, &c., sublime, as determined by an Improved Method.*

By A. Wynter Blyth.

One of the first to systematically employ sublimation as a means of recognition of the alkaloïds, &c., was Helwig (*Das Mikroscop in der Toxicologie*). His method was to place a small quantity, from a half- to a four-thousandth of a milligram, in a depression on platinum foil, cover it with a slip of glass, and then carefully heat it by a small flame. After Helwig, Dr. Guy (*Pharm. Journ. Trans.* [2], viii, 719; ix, 10, 58; *Forensic Medicine*, London, 1875) greatly improved the process by using porcelain discs, and more especially by the adoption of a convenient apparatus, which I usually call "the subliming cell." It is essentially composed of a ring of glass, from one-eighth to two-thirds of an inch in thickness, such as may be obtained by sections of tubing, the cut surfaces being ground perfectly smooth. This circle is converted into a closed cell by resting on one of the ordinary thin discs of glass used as a covering for microscopic purposes, and supporting a similar disc. The cell was placed on a brass plate provided with a nipple, which carried a thermometer, and was heated by

a small flame applied midway between the thermometer and the cell. The heat was raised very gradually, and the temperature at which any change took place was noted. In this way Dr. Guy made determinations of the subliming points of a large number of substances, and the microscopic appearances of the sublimates were described with the greatest fidelity and accuracy.

The author, on carefully repeating Dr. Guy's determinations, could not, however, in any instance agree with his subliming points; nor with the apparatus he figures and describes were any two consecutive observations found to coincide exactly. Further, on examining the various subliming temperatures of substances as stated by different authors, the widest discrepancies were found. Differences of two or even three degrees might be referred to errors of observation, a want of exact coincidence in the thermometers employed, and the like; but to what, for example, can we ascribe the irreconcileable statements which have been made with regard to theine? According to Stranch, this substance sublimes at 177°; according to Mulder, at 184·7; and that both of these observations deviate more than 70 degrees from the truth may be proved by anyone who will place a few milligrams of theine enclosed between two watch glasses over the water-bath. In a few minutes a distinct sublimate will condense on the upper glass; and in point of fact theine sublimes several degrees below 100°.

Since this great divergency of statement is not found either in the specific gravity or in the boiling points, or in any of the like determinations of the physical properties of a substance, it is selfevident that the processes hitherto used for the determination of subliming points are faulty. The sources of error are chiefly—

1. Defects in the apparatus employed, the temperature read being rather that of the metallic surface in the immediate vicinity of the thermometer than of the substance itself.

2. The want of agreement among observers as to what should be called a sublimate, one considering a sublimate only that which is evident to the naked eye, another taking cognisance of the earliest microscopic film.

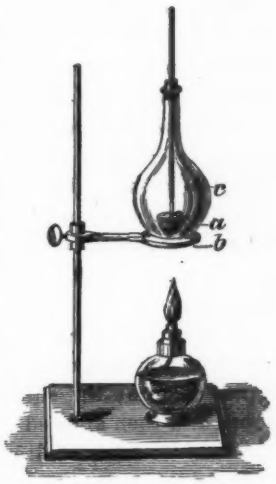
3. No two persons employing the same process.

With regard to the apparatus employed, I adopt Dr. Guy's subliming cell, but the cell, instead of resting on a metallic solid, floats on a metallic fluid. For any temperature a little above 100° this fluid is mercury, but for higher temperatures fusible metal is preferable.

The exact procedure is as follows:—

A porcelain crucible (*a*), about 3 inches in diameter, is nearly filled with mercury or fusible metal, as the case may be; a minute speck, or two or three crystals of the substance to be examined, is placed on a thin disc of microscopic covering glass, floated on the

liquid, and the cell is completed by the glass ring and upper disc. The porcelain crucible is supported on a brass plate (*b*), fixed to a retort stand in the usual way, and protected from the unequal cooling effects of currents of air by being covered with a flask (*c*), from which the bottom has been removed. The neck of the flask conveniently supports a thermometer, which passes through a cork, and the bulb of the thermometer is immersed in the bath of liquid metal. In the first examination of a substance I raise the temperature somewhat rapidly, taking off the upper disc with a forceps at every 10 degrees, and exchanging it for a fresh disc until the substance is destroyed. The second examination is conducted much more slowly, and the discs exchanged at every four or five degrees, whilst the final determination is effected by raising the temperature with great caution, and exchanging the discs at about the points of change (already partially determined).



My definition of a sublimate is this:—The most minute films, dots, or crystals which can be observed by a quarter inch power, and which are obtained by keeping the subliming cell at a definite temperature for 60 seconds.

The commencement of many sublimates assumes the shape of dots of extraordinary minuteness, quite invisible to the unaided eye; and again since the practical value of sublimation is mainly as an aid to that of the recognition of substances, if we go beyond short intervals of time the operation, otherwise simple and speedy, becomes cumbersome, and loses its general applicability.

There is also considerable discrepancy with regard to the melting point of alkaloïdal bodies; in many instances a viscous state intervenes before the final complete resolution into fluid, and one observer will consider the viscous state, while the other regards complete fluidity, as the melting point.

In the melting points given below the same apparatus was used, but the substance was simply placed on a thin disc of glass floating on the metallic bath before described—the cell not being completed—and examined from time to time microscopically, for by this means alone can the first drops formed by the most minute and closely adherent crystals to the glass be discovered.

Morphine at 150° clouds the upper disc with nebulæ; the nebulæ

are resolved by high magnifying powers into minute dots; these dots gradually get coarser, and are generally converted into crystals at 188°; the alkaloïd browns at or about 200°.

Thebaine sublimes in theine-like crystals at 135°; at higher temperatures, 160—200°, needles, cubes, and prisms were observed. The residue on the lower disc, if examined before carbonisation, is fawn-coloured, with non-characteristic spots.

Narcotine gives no sublimate; it melts at 155° into a yellow liquid, which on raising the temperature becomes continually browner to final blackness. The residue before carbonisation is a rich brown amorphous substance; but if narcotine be heated two or three degrees above its melting point, and then cooled slowly, the residue consists of long slender needles, commonly radiating from centres.

Narceine gives no sublimate; it melts at 134° into a colourless liquid, which undergoes at higher temperatures the usual transition of brown colours; the substance heated a few degrees above its melting point, and then allowed to cool slowly, shows a straw-coloured residue divided into lobes or drops, containing feathery crystals.

Papaverine gives no sublimate; it melts at 130°; the residue heated a little above its melting point, and then slowly cooled, is amorphous, of a light-brown colour, and is in no way characteristic.

Hyoscyamine gives no crystalline sublimate; it melts at 89°, and appears to volatilise in great part without decomposition; it melts into an almost colourless fluid, which when solid may exhibit a network not unlike vegetable parenchyma; on moistening the network with water, interlacing crystals immediately appear. If, however, hyoscyamine be kept at 94 or 95° for a few minutes, and then slowly cooled, the edges of the spots are arborescent, and the spots themselves crystalline.

Atropine (*Daturine*) melts at 97°; at 123° a faint mist appears on the upper disc; crystals cannot be obtained; the residue is not characteristic.

Solanine. The upper disc is dimmed with nebulæ at 190°, the sublimate being coarser and more distinct at higher temperatures. At 200° it begins to brown, and then melts; the residue consists of amber-brown non-characteristic drops.

Strychnine gives a minute sublimate of fine needles often disposed in lines at 169°; about 221° it melts; the residue (at that temperature) is resinous.

Brucine melts at 151° to a pale yellow liquid, becoming deep brown at higher temperatures; if the lower disc be examined after the melting no crystals are observed, the residue being quite transparent, with branching lines like the twigs of a leafless tree; light mists, produced

rather by decomposition than by true sublimation, condense on the upper disc at 150° and above.

Saponine neither melts nor sublimes; it begins to brown about 145°, is almost black at 185°, and quite black at 190°.

Delphinine begins to brown about 102°; at 119° it becomes amber-coloured, melts, and exhibits bubbles. There is no crystalline sublimate; the residue is not characteristic.

Pilocarpine gives a distinct crystalline sublimate at 153°, but thin mists consisting of fine dots may be observed as low as 140°. Pilocarpine melts at 159°; the sublimates at 160—170° are in light yellow drops; if these drops are heated with water and the water evaporated, feathery crystals are obtained. The residue is resinous.

Theine wholly sublimes; the first sublimate at 79° consists of minute dots; at half a degree above that temperature very small crystals may be obtained, and at such temperatures as 120° the crystals are often long and silky.

Theobromine likewise wholly sublimes; nebulæ at 134°; crystals at 170° and above.

Delphinine gives no crystalline sublimate; it begins to brown at 119°, and melts, the melted mass containing bubbles; the residue is not characteristic.

Salicine melts at 170°; it gives no crystalline sublimate; the melted mass remains almost colourless up to 180°, but above that temperature browning is evident. The residue is not characteristic.

Picrotoxine gives no crystalline sublimate; the lowest temperature at which it sublimes is 128°, the usual nebulæ then making their appearance; between 165° and 170° there is a slight browning; at 170° the substance melts; the residue slowly cooled is not characteristic.

Cantharidine sublimes very scantily between 82° and 83°; at 85° the sublimate is copious.

Quinetum begins to sublime in distinct crystals, composed of short prisms, needles, and plates at 147°; at 139° the substance is found melted in drop-like forms not crystalline; the residue from a sublimate of such temperatures as 150—163° is intermixed with well-formed crystals.

Quinidine begins to brown very slightly about 160°; if kept above that temperature up to 180° it leaves on the lower disc a rich brown residue having a peculiar reticulated appearance.

The active principles of plants may, in regard to their behaviour to heat, be classed for practical purposes into—

1. Those which give a decided crystalline sublimate:—
   (*a.*) Below 100°, *e.g.*, theine, thebaine, cantharidine.
   (*b.*) Between 100° and 150°, *e.g.*, quinetum.

(*c.*) Between 150° and 200°, *e.g.*, strychnine, morphine, pilocarpine.

2. Those which melt, but give no sublimate:—

(*a.*) Below 100°, *e.g.*, hyoscyamine, atropine.
(*b.*) Between 100° and 150°, *e.g.*, papaverine.
(*c.*) Between 150° and 200°, *e.g.*, salicin.
(*d.*) Above 200°, *e.g.*, solanine.

3. Those which neither melt nor give a crystalline sublimate, *e.g.*, saponin.

XL.—*The Alkaloïds of the Aconites.* Part III.

By C. R. Alder Wright, D.Sc. (Lond.), Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry in St. Mary's Hospital Medical School.

§ I. *Action of Saponifying Agents on Aconitine.*

As stated incidentally in Part II (this *Journal*, 1878, i, 151) saponifying agents act on aconitine in a manner perfectly parallel to their action on pseudaconitine, water being taken up, and a division into an aromatic acid and a new base being caused. Thus, with pseudaconitine—

$$C_{36}H_{49}NO_{12} + H_2O = C_9H_{10}O_4 + C_{27}H_{41}NO_9,$$

dimethylprotocatechuic acid and pseudaconine being formed. With aconitine the reaction is—

$$C_{33}H_{43}NO_{12} + H_2O = C_7H_6O_2 + C_{26}H_{39}NO_{11},$$

benzoic acid and a new base, which we propose to term *aconine*, resulting.

Moreover, just as pseudaconitine loses the elements of water, forming apopseudaconitine when heated with certain acids (*e.g.*, strong aqueous tartaric acid or dilute hydrochloric acid), so a precisely parallel change is produced in aconitine by the same treatment, *apoaconitine* being formed in virtue of the reaction—

$$C_{33}H_{43}NO_{12} = H_2O + C_{33}H_{41}NO_{11},$$

A greater or lesser quantity of the aconitine is simultaneously saponified according to the nature of the acid, inorganic acids causing tolerably rapid saponification, especially if concentrated; whilst tartaric acid is all but inert as a saponifying agent, though it acts powerfully as a dehydrating agent.

The saponifying action of alkalis on aconitine is strongly marked even in the cold; if a dilute solution of a pure aconitine salt be precipitated by excess of alkali, and the precipitate left in contact with the alkaline fluid for some days, or even hours, larger or smaller quantities of benzoic acid are easily obtained by adding to the liquid sufficient hydrochloric acid to render slightly acid, agitating with ether, and allowing the ethereal extract to evaporate spontaneously. If the alkaline liquid be warmed or heated in contact with the precipitate, the action is more rapid, whilst perfect saponification is effected by boiling aconitine for a few hours with alcoholic soda (an inverted condenser being attached); the theoretical amount of benzoic acid is obtained on evaporating off the alcohol, and treating with hydrochloric acid and ether, the ethereal solution being allowed to evaporate, and the residue being dried over sulphuric acid and weighed. Direct experiments with weighed quantities of benzoic acid showed that the whole of the acid employed could be thus regained, no loss by volatilisation of acid occurring in any but the very hottest summer weather, when a trifling daily loss in weight of the film of benzoic acid in the evaporating basin was noticed.

As with pseudaconitine (Part II) a small quantity of yellow faintly acid resinous bye-product, formed by the further action of the alkali on the aconine, accompanies the benzoic acid, the amount being greater when the saponification is effected by cohobation in an open flask than when it is performed in a sealed tube. Thus the following numbers were obtained:—

(*a.*) Aconitine from *A. Napellus* roots, worked up by Mr. Groves (Part I, this *Journal*, 1877, vol. i, 143), regenerated from recrystallised hydrobromide.

2·0560 grams gave 0·4055 gram of residue dried over sulphuric acid. On titration with decinormal soda, this neutralised alkali equivalent to 0·3906 $C_7H_6O_2$.

(*b.*) Aconitine from batch of roots worked up by Alder Wright (Part I) regenerated from recrystallised hydrobromide—

1·4780 grams gave 0·3080 gram of residue: soda neutralised on titration equivalent to 0·2924 gram $C_7H_6O_2$.

Calculated.			Found.	
			A.	B.
Benzoic acid formed per		From weight of residue	19·72	20·84
100 of aconitine	18·92	By titration.....	19·00	19·79

The slight excess thus found is clearly due to the feebly acid resinous bye-product.

The benzoic acid thus produced corresponded in all respects with

ordinary benzoic acid; the melting points of the acid from the two samples saponified as above were 120° and 120·5° respectively; the acid was volatile with the vapour of water, and crystallisable from hot water (a minute amount of tarry matter being left undissolved); from boiling light petroleum spirit it crystallised finely. Crystals thus obtained gave the following numbers:—

0·2090 gram gave 0·5215 CO_2, and 0·0935 H_2O.

	Calculated.		Found.
C_7.....	84	68·85	68·05
H_6	6	4·92	4·97
O_2.....	32	26·23	
$C_7H_6O_2$....	122	100·00	

It is worthy of notice in passing that aconitine is not the only alkaloïd which is known to form benzoic acid or a closely allied acid by an action of saponification. Thus Lossen has shown (*Liebig's Annalen*, cxxxiii, 351) that cocaïne, the alkaloïd of coca leaves, breaks up under the influence of hydrochloric acid, forming methyl chloride, benzoic acid, and ecgonine, $C_9H_{15}NO_3$ (whence presumably the formula for cocaine $(C_9H_{13}NO)\left\{\begin{matrix}O.CH_3\\O.C_7H_5O\end{matrix}\right)$. Similarly Kraut has shown (*ibid.*, cxxxiii, 87) that atropine is saponified by baryta-water, giving rise to tropine and atropic acid, apparently isomeric with cinnamic acid, and like the latter furnishing benzoic acid on oxidation.

Aconine is readily obtainable from the acid liquid from which the benzoic acid produced by saponification with alcoholic soda has been removed by ether, by rendering it alkaline with sodium carbonate, evaporating to dryness, and dissolving out with alcohol; the residue left on evaporation of the alcoholic solution is purified by solution in chloroform and evaporation of the filtered liquid, when aconine is left as a slightly coloured, extremely friable, hygroscopic and deliquescent varnish, readily soluble in water, alkalis, alcohol, and chloroform, but almost insoluble in ether, especially when free from alcohol. When thoroughly dry it does not fuse at all in the water-bath, but melts in a capillary tube to a viscid liquid at about 130°, the fusing point not being clearly defined. Neither the base nor any of its salts have as yet been obtained crystallised; its solutions are extremely bitter to the taste, but do not produce the slightest lip-tingling. A solution of the free base in water is precipitated yellow by dilute gold chloride (not in excess), the precipitate changing to black from reduction of metallic gold in a few seconds; from silver nitrate it precipitates brown silver hydrate, becoming black on warming through reduction; it reduces ammoniacal silver nitrate on boiling, but does not act immediately on

Fehling's solution; on boiling therewith for some minutes, however, a precipitate of cuprous oxide is slowly formed, the same result being brought about by digestion in the water-bath for an hour or two.

As with pseudaconitine, the action of water on aconitine is less strongly marked than that of alkalis, although of the same character; thus when aconitine is heated to 140° for 24 hours with water alone, from 80 to 90 per cent. of the base is saponified (in three experiments 15·2, 16·0, and 17·5 per cent. of benzoic acid were obtained); the benzoic acid thus produced is almost completely free from the coloured feebly acid resinous bye-product formed when alcoholic soda is employed. It is noticeable that the aconine produced under these circumstances is identical with that formed at 100°, and does not differ therefrom in that the elements of H_2O are removed at the higher temperature, as is the case with the decomposition-product of pseudaconitine (Part II), a circumstance quite in harmony with the fact that pseudaconitine loses the elements of water on heating much more readily than does aconitine. In order to procure pure aconine from the product of the action of water at 140° on aconitine, the liquid product of the heating is acidified with hydrochloric acid and agitated with ether to remove benzoic acid, then rendered alkaline with sodium carbonate and agitated again several times with ether, whereby the small quantity of unsaponified aconitine present is removed: the alkaline liquid is then evaporated to dryness, and treated with alcohol, &c., as above described.

The following numbers were obtained with two specimens of aconine:—

(A.) Prepared by saponification by alcoholic soda at 100°, 0·2987 gram gave 0·6325 CO_2, and 0·2125 H_2O.

(B.) Prepared by heating with water to 140° for 24 hours, and purifying from undecomposed aconitine as above described, 0·2725 gram gave 0·5740 CO_2, and 0·1990 H_2O.

	Calculated.		Found.	
			A.	B.
C_{26}	312	57·67	57·75	57·45
H_{39}	39	7·21	7·90	8·12
N	14	2·59		
O_{11}	176	32·53		
$C_{26}H_{39}NO_{11}$ ..	541	100·00		

0·0320 gram of specimen B, burnt in a Sprengel vacuum with oxide of copper and copper, furnished (after correction by the results of a blank experiment made simultaneously) 33·81 c.c. of CO_2 and 0·617 c.c. of N at 0° and 760 mm.; or 0·0182 gram CO_2 and 0·00077 gram N;

hence the ratio of N to CO_2 by volume is $\frac{0{\cdot}617}{33{\cdot}81} = 1$ to 54·8; whence

"Atomic" ratio of nitrogen to carbon	1 to 27·4
Calculated	1 to 26·0

These numbers represent carbon 56·9, nitrogen 2·4 per cent. by weight.

Attempts to fix the formula of aconine by the analysis of its salts led to the following results:

Mercuriodide of Aconine.—Aconine was dissolved in acetic acid, and precipitated by potassium mercuriodide; the white flocculent precipitate thus thrown down was sensibly more soluble in water than aconitine or pseudaconitine mercuriodide. After drying over sulphuric acid and finally at 100°, the following numbers were obtained with aconine prepared by saponification at 100° (A), and by water at 140° (B):—

Specimen A.	0·4725 gram	gave	0·2970 AgI.
„ „	0·4155	„	0·2570 „
„ B.	0·7215	„	0·4465 „

	Calculated for $C_{26}H_{39}NO_{11},HI,HgI_2$.	Found. A.	Found. B.
Iodine.....	33·93	33·96	33·43 33·46

Sulphate of Aconine.—A basic sulphate (or mixture of sulphate and free base) was obtained by acidulating the product of saponification with sulphuric acid, agitating with ether to remove benzoic acid, rendering slightly alkaline with sodium carbonate, evaporating to dryness, and dissolving out by absolute alcohol. After correction for a minute amount of alkaline sulphate present, this substance contained—

	Calculated for $7C_{26}H_{39}NO_{11},H_2SO_4$.	Found.
Carbon	56·22	55·51
Total hydrogen.....	7·08	7·84
H_2SO_4.....	2·52	2·35

Hydrochloride of Aconine.—Similarly a basic hydrochloride (or mixture of hydrochloride and free base) was obtained, containing—

	Calculated for $3C_{26}H_{39}NO_{11},2HCl$.	Found.
Carbon	55·19	54·88
Hydrogen	7·02	7·86
Chlorine.....	4·18	3·94

In another experiment the hydrochloric acid solution of aconine was not neutralised by sodium carbonate, but simply evaporated down in

the hope of obtaining a neutral salt; the excess of acid, however, acted on the aconine, removing the elements of water thus—

$$C_{26}H_{39}NO_{11} = H_2O + C_{26}H_{37}NO_{10} \text{ (\textit{vide} § 2)}.$$

Gold salt.—An acid solution of aconine in hydrochloric acid throws down a yellow flocculent precipitate on addition of gold chloride, which is not visibly decomposed on drying over sulphuric acid. At 100° it frits, but does not lose in weight more than a minute quantity, if previously well dried over sulphuric acid. Notwithstanding this, the precipitate appears to contain reduced gold, for different specimens contained variable percentages of metal, the lowest amount found being 23·68, higher amounts up to 30·80 and 32·62 being found in other specimens, the quantity calculated for $C_{26}H_{39}NO_{11}$, HCl, $AuCl_3$ being 22·27. The gold salt is sensibly more soluble in water than aconitine auro-chloride; an aqueous solution allowed to stand over sulphuric acid in the dark deposited a yellow resinous film containing visible particles of metallic gold.

The qualitative reactions of aconine and pseudaconine differ but little from those of their parent alkaloïds, which again are closely similar; bromine water, iodine dissolved in potassium iodide, tannin, gold chloride, mercuric iodide dissolved in potassium iodide, mercuric bromide in potassium bromide, and mercuric chloride give precipitates with nearly neutral solutions of all four bases in hydrochloric acid; these precipitates dissolve on more or less largely diluting the fluids, the aconine precipitates being more soluble than the corresponding pseudaconine ones, which again, save in the case of tannin, are markedly more soluble than those of aconitine or pseudaconitine. Other things being equal, the mercuric chloride precipitates are more soluble than those formed with mercuric bromide, which are more soluble than those thrown down by mercuric iodide. Aconine is not precipitated by sodium carbonate or ammonia, save when the solution is evaporated almost to dryness, so that an oily liquid separates along with the solid sodium or ammonium salt; pseudaconine behaves similarly, whilst aconitine and pseudaconitine are but sparingly soluble in excess of these reagents. Strong caustic potash precipitates all four bases, the aconitine and pseudaconitine precipitates being only sparingly soluble in excess, the pseudaconine being much more readily soluble on diluting the fluid, and aconine being precipitated only in very concentrated solutions. Platinic chloride throws down precipitates only with strong solutions, especially with pseudaconine and aconine, the precipitates in all cases dissolving readily on dilution.

It is noticeable that picraconitine is scarcely distinguishable from aconitine in these reactions, excepting that with sodium carbonate and ammonia it is precipitated much less readily, the precipitate being

formed only in concentrated solutions, and dissolving readily on dilution.

§ 2. *Action of Acids on Aconitine.*

Just as with pseudaconitine the action of hot mineral acids on aconitine is of the same character as that of alkalis, though not so energetic; thus a few hours heating to 100° with a slight excess of dilute sulphuric acid forms a perceptible amount of benzoic acid, whilst with a somewhat larger excess, from 15 to 40 per cent. is saponified after 12 hours' heating to 100°. On heating to 100° for one hour with concentrated hydriodic or hydrobromic acid, no methyl bromide or iodide is formed, but benzoic acid is obtainable from the product in quantity indicating the saponification of almost one half. On the other hand, a slightly acid dilute solution of aconitine hydrobromide can be kept at the ordinary temperature for months without the formation of more than inconsiderable quantities of benzoic acid; whilst aconitine may be boiled with a large excess of concentrated tartaric acid solution without the formation of more than traces of benzoic acid (although dehydration is thus brought about); whence the advantage of tartaric acid over mineral acids for acidulating the alcohol in the first process of treating the aconite roots for extraction of alkaloïds.

Thus the following numbers were obtained from this product of dehydration of aconitine formed by heating the base to 100° for eight hours with about 15 parts of nearly saturated tartaric acid solution; the cooled liquid was agitated with ether, which removed a trace of resinous bye-product, and then treated with sodium carbonate and ether: the base which crystallised from the ethereal solution was purified by conversion into nitrate, crystallisation of that salt, and decomposition by alkali and crystallisation from ether; the crystals were anhydrous.

0·2895 gram gave 0·6710 CO_2, and 0·1950 H_2O.

	Calculated.		Found.
C_{33}	396	63·16	63·21
H_{41}	41	6·54	7·48
N.....	14	2·23	
O_{11}	176	28·07	
$C_{33}H_{41}NO_{11}$....	627	100·00	

The gold salt gave the following numbers:—

0·3430 gram gave 0·0695 Au. Au = 20·26 per cent.
Calculated for $C_{33}H_{41}NO_{11}$, HCl, $AuCl_3$ = 20·29 „

The hydrobromide of this base crystallised well, and contained $2\frac{1}{2}$ H_2O like the analogous salt of aconitine; it seemed, however, to be more soluble in water than aconitine hydrobromide.

0·9600 gram of air-dry crystals lost at 100° 0·0610 gram ..... = 6·35 per cent.
Calculated for $C_{33}H_{41}NO_{11}$, HBr, $2\frac{1}{2}H_2O$ .... = 5·97 „

The pure base melts first completely at 185—186°, slightly fritting a few degrees below this temperature; when examined side by side with aconitine (melting point 183—184°*), it is distinctly seen that aconitine melts first by 1—2°. In physiological potency it appears, from the effects experienced whilst working with it, to be not inferior to aconitine.

Continued boiling with dilute sulphuric acid gives rise to a large amount of apoaconitine. Aconitine was boiled with 20 parts of 5 per cent. acid for 12 hours, an inverted condenser being attached. From the amount of benzoic acid formed it appeared that about one-third of the base was saponified; on adding sodium carbonate to the liquid freed from benzoic acid by ether, a copious precipitate was thrown down, whilst aconine remained in solution; the precipitate was dissolved in ether, and crystallised by spontaneous evaporation; the crystals were anhydrous, melted at 184—185°, and gave the following numbers:—

0·2525 gram gave 0·5890 CO_2 and 0·1710 H_2O.
0·4070 „ of gold salt gave 0·0835 Au.

Calculated for $C_{33}H_{41}NO_{11}$.		Found.
Carbon in base	63·16	63·59
Hydrogen in base.....	6·54	7·52
Gold in gold salt	20·29	20·51

It would seem highly probable from these results that in the process of extracting aconitine from aconite roots, partial dehydration of the alkaloïd takes place (as with pseudaconitine—Part II), so that the base ultimately obtained by crystallisation from ether, &c., consists of a mixture of aconitine and apoaconitine: that this is so, is indicated by the results obtained in Part I with two different specimens: one a mixture of nitrates from *A. Napellus* obtained by Mr. T. B. Groves in 1860 (A), the other a specimen of base crystallised from ether isolated by one of us from *A. Napellus* products worked up by Mr. Groves in 1874 (B).

* In Part II, through an uncorrected error of the press, 189° is given as the melting point.

	Calculated.		Found.		
	For $C_{33}H_{43}NO_{12}$.	For $C_{33}H_{41}NO_{11}$.	A.		B.
Carbon....	61·39	63·16	62·75	62·90	62·90
Hydrogen	6·67	6·54	7·24	7·30	7·45

That the latter specimen was really a mixture of aconitine and apoaconitine is shown by the fact that (as described in Part I) it furnished pure aconitine (C = 61·78; H = 6·78) on conversion into hydrobromide, recrystallisation of this salt, and regeneration, the more soluble hydrobromide of apoaconitine being thus removed.

It is worthy of notice in this connection that the action of acids on aconine appears to be parallel to that on aconitine, dehydration taking place in accordance with the reaction—

$$C_{26}H_{39}NO_{11} = H_2O + C_{26}H_{37}NO_{10},$$

for in an attempt to prepare aconine hydrochloride by acidulating slightly with hydrochloric acid the product of the action of water in sealed tubes at 140° for 24 hours on aconitine, agitating with ether to remove benzoic acid, and evaporation to dryness, there was obtained a varnish-like salt readily soluble in water, not precipitable from the solution by alkalis, and of bitter taste: on analysis this gave numbers agreeing with the formula, $C_{26}H_{37}NO_{10}.HCl$, indicating that the elements of water had been removed from the aconine by the slight excess of hydrochloric acid during evaporation.

0·2685 gram gave 0·5470 CO_2 and 0·1995 H_2O.
0·3870 „ 0·1080 AgCl.

	Calculated.		Found.
C_{26}	312	55·77	55·56
H_{38}	38	6·79	8·25
N	14	2·50	—
O_{10}	160	28·60	—
Cl	35·5	6·34	6·51
$C_{26}H_{37}NO_{10}.HCl$..	559·5	100·00	

§ 3. *Action of Organic Anhydrides on Aconitine, Aconine, and Pseudaconine.*

(A.) *Action of Benzoic and Acetic Anhydrides on Aconitine and Aconine.*

The experiments described in Part II, made with pseudaconitine were repeated with aconitine, with the result of bringing about perfectly parallel reactions; thus aconitine and benzoic anhydride react on

one another, eliminating water and forming a benzoylated base, *benzoyl apoaconitine*—

$$C_{33}H_{43}NO_{12} + 2(C_7H_5O)_2O = 3C_7H_6O_2 + C_{33}H_{40}(C_7H_5O)NO_{11}.$$

Similarly, acetic anhydride forms the corresponding *acetyl-apoaconitine*—

$$C_{33}H_{43}NO_{12} + 2(C_2H_3O)_2 = 3C_2H_4O_2 + C_{33}H_{40}(C_2H_3O)NO_{11}.$$

The benzoylated base gave the following numbers:

0·2510 gram gave 0·5995 CO_2 and 0·1570 H_2O.

	Calculated.		Found.
C_{40}	480	65·66	65·13
H_{45}	45	6·16	6·95
N	14	1·92	
O_{12}	192	26·26	
$C_{33}H_{40}(C_7H_5O)NO_{11}$	731	100·00	

0·4240 gram of gold salt dried over sulphuric acid gave 0·0785 Au ..... = 18·51 per cent.
Calculated for $C_{40}H_{45}NO_{12}.HCl.AuCl_3$ .... = 18·32 „

0·1870 gram of base saponified with alcoholic potash gave 0·062 gram of benzoic acid with a trace of resin; by titration = 0·061 of $C_7H_6O_2$.

	Calculated.	Found.	
		By weighing.	By titration.
Benzoic acid	33·4	33·2	32·6

Since benzoic acid is furnished by aconitine itself, *two* equivalents of that acid are produced by benzoyl apoaconitine.

Acetyl-apoaconitine furnished the following numbers:

0·2415 gram gave 0·5600 CO_2, and 0·1600 H_2O.

	Calculated.		Found.
C_{35}	420	62·78	63·22
H_{43}	43	6·43	7·36
N	14	2·09	
O_{12}	192	28·70	
$C_{33}H_{40}(C_2H_3O)NO_{11}$	669	100·00	

On saponification and distillation of the product with dilute sulphuric acid, a distillate was obtained containing acetic and a little benzoic acid. This distillate was titrated with soda, and the benzoic acid contained was removed by means of hydrochloric acid and ether; the benzoic acid left in the distilling flask was similarly extracted;

ultimately 0·3755 gram of base furnished 0·040 acetic acid, and 0·069 benzoic acid (that from distillate being 0·016 gram, and that from residue 0·053 gram).

	Calculated.	Found.
Benzoic acid.....	18·2	18·4
Acetic acid	9·0	10·6
Total acid	27·2	29·0

Acetyl-apoaconitine readily crystallises from ether in small anhydrous crystals, readily soluble in acids; crystallised salts, however, were not formed on spontaneous evaporation of the solutions, but only varnishes, even with the nitrate and hydrobromide. When contrasted with aconitine, it melts distinctly some 3—4° lower, at 180—181° (corrected). It is essential that a temperature not higher than 100° should be employed in its preparation, otherwise its acetate decomposes, forming an amorphous base of higher carbon percentage; thus the base obtained in an experiment in which 1 part of aconitine and 2 of acetic anhydride were heated to 115° for an hour, wholly refused to crystallise from ether or alcohol, and contained carbon 65·08, 65·58, hydrogen, 7·60, 7·90.

The formation of these derivatives shows that aconitine possesses a "structure" perfectly parallel to that of pseudaconitine; taking these substances into consideration, together with the results obtained by saponification (§ 1), the following formulæ are arrived at:—

Aconitine ..... $(C_{26}H_{35}NO_7)\begin{cases}OH\\OH\\OH\\O.CO.C_6H_5\end{cases}$

Apoaconitine ..... $(C_{26}H_{35}NO_7)\begin{cases}O\\OH\\O.CO.C_6H_5\end{cases}$

Aconine ..... $(C_{26}H_{35}NO_7)\begin{cases}OH\\OH\\OH\\OH\end{cases}$

Apoaconine..... $(C_{26}H_{35}NO_7)\begin{cases}O\\OH\\OH\end{cases}$

Benzoyl-apoaconitine.. $(C_{26}H_{35}NO_7)\begin{cases}O\\O.CO.C_6H_5\\O.CO.C_6H_5\end{cases}$

Acetyl-apoaconitine .. $(C_{26}H_{35}NO_7)\begin{cases}O\\O.CO.CH_3\\O.CO.C_6H_5.\end{cases}$

It should hence result that if aconine be acted on by benzoic anhydride, there should be formed either a tetrabenzoyl-aconine, or a dibenzoylated apoaconine identical with the above "benzoyl-apoaconitine," the latter of which is more probable, as aconine appears to be readily dehydrated under certain conditions (§ 2). On treating aconine with twice its weight of benzoic anhydride, and proceeding as described in Part II, a base was formed readily precipitable by sodium carbonate, and apparently identical with the benzoyl-apoaconitine prepared from aconitine.

0·2630 gram gave 0·6245 CO_2, and 0·1610 H_2O.

Calculated for $C_{33}H_{40}(C_7H_5O)NO_{11}$.		Found.
Carbon.....	65·65	64·75
Hydrogen	6·16	6·80

0·2860 gram of gold salt dried over sulphuric acid gave 0·053 Au = 18·53 per cent.

0·2405 gram of gold salt dried over sulphuric acid gave 0·0445 Au = 18·50 per cent.

Calculated for $C_{40}H_{45}NO_{12}.HCl.AuCl_3$ = 18·32 per cent.

0·2390 gram saponified gave 0·081 of benzoic acid, containing a little resin; by titration = 0·076 $C_7H_6O_2$.

	Calculated.	Found.	
		By weighing.	By titration.
Benzoic acid.....	33·4	33·9	31·8

Neither this product nor the body from aconitine crystallised distinctly, although indications of crystallisation were in each case observed in the flakes that separated on spontaneous evaporation of the ethereal solution to which light petroleum distillate had been added. Each base began to frit and soften in a capillary tube at near 130°, but did not become completely fluid till between 150° and 160°, the fusing points being extremely indistinctly marked. On stirring with dilute nitric acid, almost insoluble nitrates were formed, not in crystals, but in thick, white, nearly transparent masses, resembling softened fragments of gum. The gold salts were not crystalline, and did not crystallise from alcohol. No perceptible difference in any respect between the two specimens was recognisable, whence their identity would seem beyond dispute: hence, during the transformation of aconitine into aconine no isomeric change (like that of quinine into quinicine) would seem to be produced; for the production of acetyl apoaconitine does not appear markedly to change the physical characters, whence presumably the radicle $C_{26}H_{35}NO_7$ is not materially affected during the change; by analogy it is not affected in the production of benzoyl-

apoaconitine, which consequently has that radicle in the same condition as both aconine and aconitine.

(B.) *Action of Benzoic and Acetic Anhydrides on Pseudaconine.*

In order to compare with these results the action of organic anhydrides on pseudaconine, that base was heated to 100° with twice its weight of benzoic and acetic anhydrides respectively for three hours: in the former case, in order to render the whole readily fluid at 100°, a portion of benzoic anhydride was employed, obtained as a slightly impure substance, distilling last during the preparation of the anhydride from benzoyl chloride and sodium benzoate, and containing a minute quantity of some fluid substance of high boiling point, the presence of which caused the anhydride to be slightly pasty at the ordinary temperature, and fluid at 100°. After extracting the new bases formed as described in Part II for the analogous pseudaconitine derivatives, ethereal solutions were obtained which, on spontaneous evaporation, left varnishes which would not crystallise from ether, alcohol, or ether-petroleum; no crystallised salts, also, were obtainable from either base. The following values were obtained, showing that the products found were respectively *dibenzoyl-apopseudaconine*, $(C_{27}H_{37}NO_5)\begin{matrix}=O\\ O.C_7H_5O\\ O.C_7H_5O\end{matrix}$, and *diacetyl-apopseudaconine*,—

$$(C_{27}H_{37}NO_5)\begin{matrix}=O\\ O.C_2H_3O,\\ O.C_2H_3O\end{matrix}$$

the correlatives of the benzoyl apoaconitine (dibenzoyl-apoaconine) just described, formed in virtue of the reactions—

$$C_{27}H_{41}NO_9 + 3(C_2H_3O)_2O = 4C_2H_4O_2 + C_{27}H_{37}(C_2H_3O)_2NO_8,$$
$$C_{27}H_{41}NO_9 + 3(C_7H_5O)_2O = 4C_7H_6O_2 + C_{27}H_{37}(C_7H_5O)_2NO_8.$$

0·2585 gram of the benzoylated product gave 0·6465 CO_2, and 0·1825 H_2O.

	Calculated.		Found.
C_{41}	492	68·99	68·20
H_{47}	47	6·61	7·84
N	14	1·96	
O_{10}	160	22·44	
$C_{27}H_{37}(C_7H_5O)_2NO_8$..	713	100·00	

0·5835 gram gave on saponification 0·2005 of benzoic acid, containing a little resinous matter; by titration this = 0·1965 $C_7H_6O_2$.

	Calculated.	Found. By weighing.	Found. By titration.
Benzoic acid.....	34·2	34·3	33·7

0·2520 gram of acetylated product gave 0·5840 CO_2, and 0·1855 H_2O.

	Calculated.		Found.
C_{31}.....	372	63·16	63·20
H_{43}.....	43	7·30	8·17
N	14	2·38	
O_{10}.....	160	27·16	
$C_{27}H_{37}(C_2H_3O)_2NO_8$..	589	100·00	

0·6040 gram saponified with standard soda formed acetic acid, neutralising soda equivalent to 0·1250 $C_2H_4O_2$; on acidulating and distilling, an acid distillate was obtained, neutralising soda = 0·1190 $C_2H_4O_2$.

	Calculated.	Found. First titration.	Found. From distillate.
Acetic acid.....	20·4	20·7	19·7

Dibenzoyl apopseudaconine is almost insoluble in water, in this respect differing greatly from pseudaconine and apopseudaconine; a solution of this base in weak acids precipitates with sodium carbonate, ammonia, or caustic potash, just like pseudaconitine, the precipitate not being very readily dissolved on dilution; it fuses in the water-bath. Diacetyl apopseudaconine also melts below 100°; it is slightly soluble in water, forming an alkaline fluid, though less readily soluble than pseudaconine; solutions of its salts are not precipitated at all by sodium carbonate, whilst ammonia gives a precipitate readily soluble on dilution, and caustic potash a precipitate soluble on large dilution.

Attempts to prepare these two derivatives by fusing pseudaconine with benzoic or acetic anhydride at 120—130°, did not give good results, the higher temperature decomposing the new bases almost as quickly as formed, so that on extracting the substances ultimately obtained, and saponifying them, much smaller quantities of benzoic and acetic acids were formed than corresponded with bodies produced at 100°; on combustion the products gave numbers which, together with the results of titration, indicated that these products were mixtures of apopseudaconine with from about 50 to 100 per cent. of its weight of the dibenzoylated or acetylated derivatives above described. For this reason, probably, attempts to form dibenzoyl-apopseudaconine by fusing together pseudaconine and benzoic acid at a temperature as little above 100° as possible, gave but little result; on dissolving the fused mass (after some hours action) in alcohol, adding aqueous tartaric acid and ether, and shaking, and adding sodium carbonate to

the acid tartrate solution thus obtained, a small quantity of a white flocculent precipitate was formed, which appeared to be identical in all respects with the dibenzoyl apopseudaconine above described, and which especially formed benzoic acid copiously on saponification: the amount of this substance obtained was too small for complete examination, but there can be little doubt that it was actually dibenzoyl apopseudaconine, formed by the reaction:—

$$C_{27}H_{41}NO_9 + 2C_7H_6O_2 = 3H_2O + C_{27}H_{37}(C_7H_5O)_2NO_8.$$

Attempts to synthesise pseudaconitine or apopseudaconitine by a parallel reaction by fusing together pseudaconine with small quantities of dimethyl-protocatechuic acid (so that the melting point should be as little as possible above 100°) similarly led to no marked results; minute quantities of a base (presumably apopseudaconitine) precipitable by sodium carbonate were formed, but the yield was too small for the obtaining of any analytical numbers.

§ 4. *Decomposition-products of Picraconitine.*

The quantity of picraconitine, $C_{31}H_{45}NO_{10}$ (Part I), at our disposal being very small, we were unable to work out the character of its decomposition-products and derivatives as thoroughly as we could have wished, but we have managed to obtain evidence that this base is constituted similarly to the other two, pseudaconitine and aconitine, already examined, being more closely allied to the latter, inasmuch as it furnishes *benzoic acid* on saponification, the action being—

$$C_{31}H_{45}NO_{10} + H_2O = C_7H_6O_2 + C_{24}H_{41}NO_9.$$

The complementary product, which we propose to term *picraconine*, is so extremely similar to aconine in all respects, that the only really marked difference observable is in the numbers obtained on analysis, and even in this case the difference is not great: picraconine also appears to be slightly less difficultly soluble in pure ether than aconine.

0·555 gram of picraconitine saponified by alcoholic soda gave of benzoic acid containing a little resin 0·1170 gram; by titration this was equivalent to 0·1105 $C_7H_6O_2$.

0·2880 gram heated to 140° with water in a sealed tube for 24 hours gave of almost absolutely pure benzoic acid 0·0555 gram.

	Calculated.	Found.	
		By weighing.	By titration.
Benzoic acid.....	20·6	21·6	19·9
		19·3	—

The benzoic thus obtained was recognised by its physical properties

and qualitative tests; after crystallisation from water it melted at 120—121°.

The complementary product, picraconine, was isolated as described in the case of aconine (§ 1); neither the base nor any salt could be crystallised.

0·2770 gram gave 0·5945 CO_2, and 0·214 H_2O.

	Calculated.		Found.
C_{24}.....	288	59·14	58·53
H_{41}.....	41	8·42	8·58
N	14	2·87	—
O_9	144	29·57	—
$C_{24}H_{41}NO_9$..	487	100·00	

The mercuriodide gave these numbers,—

0·2220 gram gave 0·1470 AgI I = 35·78 per cent.
Calculated for $C_{24}H_{41}NO_9,HI,HgI_2$ = 35·64 „

Hence picraconitine may be written $(C_{24}H_{40}NO_8)—O—CO.C_6H_5$; from want of material we were unable to find out whether this formula should be further dissected into $(C_{24}H_{37}NO_5)\begin{cases}OH\\OH\\OH\\O.CO.C_6H_5\end{cases}$, parallel to aconitine and pseudaconitine.

§ 5. *Alkaloïd Constituents of Aconite Roots generally.*

The experiments above described, and those contained in Parts I and II, indicate that, whilst the roots of *Aconitum ferox* contain, as chief essential crystallisable constituent, pseudaconitine yielding dimethyl-protocatechuic acid on saponification, those of *A. Napellus* contain bases which yield benzoic acid, some batches of *Napellus* roots containing only aconitine as crystallisable alkaloïd, whilst one batch also contained picraconitine. Either from admixture of small quantities of one kind of root with another, or from the presence of small amounts of different alkaloïds, in addition to the main bases present, small but perceptible quantities of dimethyl protocatechuic acid have been obtained from the crude alkaloïdal mixture of bases isolated from *A. Napellus;* whilst conversely, minute amounts of benzoic acid have been obtained from the alkaloïds of *A. ferox;* but the quantities of the second saponification-acids thus obtained were in every case respectively so small that practically each species is distinguished by containing a base peculiar to itself.

Besides crystallisable alkaloïds, however, considerable amounts of

non-crystalline bases are uniformly obtained during the process of extraction, though whether these pre-exist as such, or are formed during the process of isolation, is open to question, especially as it has been noticed that the amount of crystallisable alkaloïds relatively to the non-crystalline bases obtainable from a given batch of roots, varied from 60 of the first and 40 of the second, to 20 of the first and 80 of the second, according as the alcohol employed was acidulated with tartaric or with sulphuric acid. On examination of the non-crystalline bases, they uniformly furnish numbers quite compatible with the notion that they are formed from the crystallisable bases by saponification, dehydration, polymerisation, &c., changes to which alkaloïds as a class appear to be peculiarly prone. This has been already shown in the case of the amorphous bases from *A. ferox* (Part II); the following numbers demonstrate that the same is true for the analogous substances derived from *A. Napellus*.

Two distinct batches of amorphous bases were obtained from the 2 cwt. of *A. Napellus* roots worked up as described in Part I. One of these (A) was the inspissated ethereal mother-liquor obtained by crystallising the precipitate thrown down by sodium carbonate from the aqueous solution of tartrates got by percolating with alcoholic tartaric acid, evaporating off alcohol from the percolate, adding water, and straining from resin. The other (B) was got from the filtrate from the precipitate thrown down by sodium carbonate, by adding mercuriodide of potassium, collecting the precipitate, suspending in alcohol, decomposing by sulphuretted hydrogen, and shaking the resulting hydriodide solution (freed from alcohol by evaporation) with caustic soda and ether, whereby almost all the bases present were dissolved. No crystallisable salts were obtainable from either batch. On dissolving in acid and pouring into excess of sodium carbonate solution, a thick precipitate of white flakes was in each case thrown down, whilst there remained in the alkaline solution a notable quantity of alkaloïd, apparently somewhat impure apopseudaconine, inasmuch as on evaporating to dryness and treating with alcohol, a base was dissolved out mostly soluble in water and giving the following values:—

	Calculated for $C_{27}H_{39}NO_8$.	Found.	
		A.	B.
Carbon.....	64·16	64·12	63·38
Hydrogen	7·72	8·14	8·03
Nitrogen.....	2·77	2·86	2·77

The precipitated flakes gave these percentages:—

	A.	B.
Carbon	65·83	65·46
Hydrogen.....	7·78	7·58
Nitrogen	2·71	3·05
Benzoic acid formed on saponification: by weighing	—	15·3
by titration	14·4	14·1

The benzoic acid thus formed contained in each case a minute quantity of dimethylprotocatechuic acid.

According to Hübschmann (*Jahresber.*, 1857, 416), commercial so-called "aconitine" (query from *A. ferox*, *A. Napellus*, or a mixture) sometimes contains a non-crystalline alkaloïd, sparingly soluble in ether, more readily soluble in water and alcohol than aconitine, bitter, not precipitated by ammonia. To this he applied the term *napelline*. Subsequently he regarded "napelline" as identical with an amorphous body termed by him *acolyctine*, obtained from *A. Lycoctonum* by the old process of treatment (which involved prolonged contact with hot and cold mineral acids and alkalis, or lime), and separated from another body, "lycoctonine," by means of ether, which dissolves the latter. The descriptions given of acolyctine (or napelline) render it highly probable that this body was a decomposition-product, as its general characters are precisely those of aconine and picraconine. According to Flückiger (*Jahresber.*, 1870, 837), "lycoctonine" can be crystallised, and melts at 100—104°, whence its essential identity with pseudaconitine is probable, the substance described by many chemists and pharmacists as "lycoctonine" being, however, apparently anything but pure, no doubt containing much pseudaconine (and other alteration-products) from the modes of extraction adopted.

How far the "atisine" of Broughton, isolated by him from *A. heterophyllum* (*Med. Press and Circular*, May 24, 1874), and described as indicated by $C_{46}H_{74}N_2O_5$, and being simply a bitter tonic, is related to the other aconite alkaloïds is open to question. The description of the alkaloïd would rather suggest a resemblance to "jervine" from *Veratrum album*, the alkaloïds of which we are now investigating.

In 1864 T. and H. Smith stated that they obtained from *fresh* juice of *A. Napellus* roots an alkaloïd which appeared to be *narcotine*, and which they termed "aconelline." The occurrence of this base has not been confirmed, but it is noteworthy that there is a sort of connection between narcotine and pseudaconitine, each being capable of saponification, the latter forming dimethylprotocatechuic acid, $C_6H_3\begin{cases}O.CH_3\\O.CH_3\\CO.OH\end{cases}$,

the former opianic acid, or dimethyl protocatechuic acid, in which H is replaced by COH, viz., $C_6H_2\begin{cases}O.CH_3\\O.CH_3\\CO.OH\\COH\end{cases}$ (this Journal, 1876, i, 173, 281).

§ 6. *Summary of Results obtained in Parts I, II, and III.*

(1.) *A. ferox* roots are characterised by containing a crystallisable, highly active alkaloïd, pseudaconitine, $C_{36}H_{49}NO_{12}$, together with apparently less active amorphous bases, not improbably formed from pseudaconitine during extraction. The salts of this base do not crystallise readily as a class, but certain of them, *e.g.*, the aurochloride and the nitrate, are crystallisable. The base crystallises with H_2O, and fuses at a few degrees above 100°.

(2.) *A. Napellus* roots contain as chief active constituent a crystallisable base, aconitine, $C_{33}H_{43}NO_{12}$, together with less active amorphous bases, probably formed therefrom during extraction. One batch of roots, and only one (query, consisting solely of *A. Napellus* roots), yielded, in addition to aconitine, another base, not crystallisable, but forming well crystallised salts. This alkaloïd, picraconitine, is far less physiologically active than aconitine, being comparatively quite inert. Aconitine fuses at about 184°, and forms well crystallised salts. It crystallises anhydrous from ether, alcohol, &c.

(3.) Pseudaconitine and aconitine readily lose the elements of water, forming apo-derivatives, closely resembling the original bases in all respects, viz., apopseudaconitine, $C_{36}H_{47}NO_{11}$, and apoaconitine, $C_{33}H_{41}NO_{11}$. This action is readily brought about by prolonged contact with hot acid solutions; accordingly it is difficult to obtain either parent base pure. The salts of the apo-derivatives (nitrates, hydrobromides, &c.), though closely resembling those of the parent bases, are apparently somewhat more soluble, so that the parent bases can be freed from small admixtures of apo-derivatives by conversion into a salt, recrystallising, and regenerating. This, however, is not possible with the gold salts, the aurochlorides of the apo-derivatives crystallising out into those of the parent bases.

(4.) On treatment with saponifying agents, aconitine, pseudaconitine, and picraconitine break up, in accordance with the equation—

$$(M).OX + H_2O = HOX + (M).OH$$

(where X is an acid radicle), forming either benzoic acid or an acid derivative thereof, and new bases respectively, aconine, $C_{26}H_{39}NO_{11}$, pseudaconine, $C_{27}H_{41}NO_9$, and picraconine, $C_{24}H_{41}NO_9$. Aconine and picraconine are extremely alike, and have not yet been obtained crys-

talline; they are insoluble in ether (or nearly so), in which pseudaconine readily dissolves. This latter can be crystallised, though with difficulty. Hübschmann's "napelline" and "acolyctine" were probably one or other of these bodies.

(5.) On treatment with organic anhydrides (benzoic, acetic), aconitine and pseudaconitine lose the elements of water and form derivatives in which H is replaced by an acid radicle. The general reaction is—

$$(N)\begin{matrix}OH\\OH\\OH\\OX\end{matrix} + 2Y_2O = 3HOY + (N)\begin{matrix}O\\OY,\\OX\end{matrix}$$

where (N) is a nitrogenous radicle, different for each base, and Y_2O an organic anhydride.

Pseudaconitine (and probably the others) forms analogous derivatives by the action of organic acids, thus—

$$(N)\begin{matrix}OH\\OH\\OH\\OX\end{matrix} + YOH = 2H_2O + (N)\begin{matrix}O\\OY.\\OX\end{matrix}$$

(6.) Aconine and pseudaconine form analogous derivatives by the action of organic anhydrides—

$$(N)\begin{matrix}OH\\OH\\OH\\OH\end{matrix} + 3Y_2O = 4YOH + (N)\begin{matrix}O\\OY,\\OX\end{matrix}$$

whilst it is probable that organic acids can also produce analogous reactions, indications of such having been obtained in the case of pseudaconine—

$$(N)\begin{matrix}OH\\OH\\OH\\OH\end{matrix} + 2YOH = 3H_2O + (N)\begin{matrix}O\\OY.\\OY\end{matrix}$$

(7.) Certain acids, however, under certain conditions, only transform aconine and pseudaconine into apo-derivatives—

$$(N)\begin{matrix}OH\\OH\\OH\\OH\end{matrix} = H_2O + (N)\begin{matrix}O\\OH,\\OH\end{matrix}$$

this reaction being precisely similar to that whereby apoaconitine and apopseudaconitine are formed, viz.:—

$$(N)\begin{matrix}OH\\OH\\OH\\OX\end{matrix} = H_2O + (N)\begin{matrix}O\\OH.\\OX\end{matrix}$$

(8.) So far as the preparation of aconite alkaloïds for medicinal purposes is concerned, there is no particular difficulty in obtaining well crystallised salts and bases from either *A. Napellus* or *A. ferox*. As the amorphous precipitated substances at present sold as so-called "aconitine" are liable to vary much in composition and physiological potency, owing to the presence of variable quantities of less active amorphous bases (probably formed during extraction by various changes), the use of such substances should be discontinued, and that of the crystallised alkaloïds and their salts substituted. The cost, however, of manufacturing the crystallised substances would be much greater than that of making the present amorphous substances, partly on account of the waste of ether, &c., in crystallising, and the greater amount of labour required, partly on account of the diminished yield due to the exclusion of the non-crystalline bodies. As it does not seem that the apo-derivatives are in any way inferior to the parent bases in physiological power, it would not be necessary to separate these bodies.

XLI.—*The Alkaloïds of the Veratrums.* Part I. *The Alkaloïds of Veratrum Sabadilla* (Asagrœa officinalis).

By C. R. Alder Wright, D.Sc. (Lond.), Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry in St. Mary's Hospital Medical School.

§ 1. *General History of the Alkaloïds.*

The alkaloïdal constituents of *Veratrum Sabadilla* seeds have been partially investigated by various chemists and pharmacists, with results in many respects contradictory of each other. On examining the methods of manipulation adopted by most of these experimenters for the purpose of isolating the alkaloïds contained in the seeds, it is at once manifest that if any alkaloïd be naturally present which is capable of splitting up by saponification, like the aconite alkaloïds, this base must inevitably have been more or less decomposed during extraction by the reagents employed in many instances; consequently there is room for some doubt as to how far the substances isolated and examined by different investigators were normal constituents of the seeds, and how far they were alteration-products or mixtures. On subjecting a specimen of commercial so-called "veratria" from saba-

dilla seeds, obtained from Messrs. Hopkin and Williams, to the action of alcoholic soda at 100°, or of water in sealed tubes at 140°, we found that considerable quantities of *two* different acids were formed, one identical with the *dimethylprotocatechuic acid* obtained by us from pseudaconitine (this Journal, 1878, i, 151), and therefore identical with the *veratric acid* obtained by E. Merck from sabadilla seeds (Körner, *Deut. Chem. Ges. Ber.*, 1876, 937), the other apparently identical with the *methylcrotonic acid* synthesised by Frankland and Duppa (this Journal, 1865, 133), and with the *cevadic acid* of Pelletier and Caventou (*Ann. Chem. Phys.* [2], 14—69), from which it is probable that the so-called "veratria" of commerce is a mixture containing two different saponifiable alkaloïds (and possibly others besides), so that a ready explanation is offered as to why such divergent results have been obtained by different experimenters hitherto.

Thus Pelletier and Caventou obtained in 1819 an amorphous base (mixture ?) melting at 50° (*Ann. Chim. Phys.* [2], 14, 69), whilst Couerbe obtained in 1834 (*ibid.* [2], 52, 352) three alkaloïdal bodies, of which one was amorphous, but yielded a crystallisable sulphate and hydrochloride. This was insoluble in water, melted at 115°, and was termed by him *veratrine*. The second was soluble in water and crystallisable therefrom, and fusible at 200°: this he termed *sabadilline*. The third was soluble in water, and non-crystalline, and was viewed by him as a *hydrate of sabadilline*. In 1855 Merck isolated from the amorphous mixture then sold as "veratria" a small quantity of a crystallisable alkaloïd, the salts of which, with the exception of the aurochloride, did not crystallise. To this Merck applied the term *veratrine*, although it in no way corresponded with the base previously described by Couerbe under that name. He ascribed to it the formula $C_{32}H_{52}N_2O_8$ (*Liebig's Annalen*, xcv, 200).

In 1871 Weigelin, working in Dragendorff's laboratory, described three alkaloïds as obtainable from *V. Sabadilla* (*Untersuchungen über die Alk. der Sabadillsamen*, Dissert. Dorpat, 1871; also Dragendorff, *Beiträg. z. ger. Chemie*, 1872, 94; *Wigger's and Husemann's Jahresber. der Fortschr. der Pharmacie*, 1871, 28; *N. Jahresber. Pharm.*, xxxvii, 94). One of these fused at 150°, and was regarded by Weigelin and Dragendorff as Merck's base; they obtained numbers leading to the formula, $C_{52}H_{86}N_2O_{15}$. The other two were obtained by shaking with fusel-oil the liquid from which ammonia had precipitated the first base; of these one was almost insoluble in ether, but crystallised from benzene; as it was somewhat soluble in water, and fused at 200°, they viewed it as Couerbe's sabadilline; the other was amorphous, and more soluble in water than sabadilline; it formed only amorphous salts; to this they applied the term *sabatrine*, regarding it as a simple

substance. The analytical numbers led to the formulæ, $C_{41}H_{66}N_2O_{13}$ and $C_{51}H_{86}N_2O_{17}$ for these bases respectively. Moreover, Weigelin regarded the first base, the veratrine of Merck, as being capable of existing in more than one modification, one soluble in water, one insoluble therein, or nearly so.

Recently (*Liebig's Annalen*, clxxxv, 224) Schmidt and Köppen have obtained from sabadilla seeds a base crystallisable from alcohol, and melting at 205°; this they regard as identical with Merck's base, but they assign to it the formula, $C_{32}H_{50}NO_9$; they conclude with Weigelin, that this base can exist as a modification soluble in water, as well as in two insoluble forms, one crystalline, one amorphous.

On comparing together the analytical data and general collateral evidence contained in these various papers, it is evident that whilst Merck had obtained the base described by him as "veratrine," in a state of tolerable purity, this body was not identical with that previously described by Couerbe, under the same name; and that his formula was incorrect, the single nitrogen determination on which it was founded being erroneous: for Schmidt and Köppen had evidently the same body in their hands, and all Merck's analyses (with the exception of this solitary nitrogendetermination) agree sharply with those of Schmidt and Köppen, which again agree well with their formula, and equally well with the almost identical formula, *à priori* more probable, which, as shown below we deduce from our experiments, together with those of these chemists, viz., $C_{32}H_{49}NO_9$.

Next it is evident from Weigelin's statement as to the melting point of his "veratrine," and his analytical numbers, that, whilst he had obtained the same alkaloïd as Merck, and Schmidt and Köppen, it was in a very defective state of purity. The "sabadilline" of Weigelin agrees in characters with the base described under that name by Couerbe; it is remarkable, however, that neither from sabadilla seeds nor from a sample of what is sold as "sabadilline" commercially (obtained from Messrs. Burgoyne and Burbidges, agents for Kahlbaum and Co.), could we isolate any base possessing these characters, although we obtained from each source an alkaloïd agreeing with "sabadilline," in the physical property of very sparing solubility in ether, but furnishing on analysis numbers very different from those of Weigelin. As to the "sabatrine" of Weigelin, our own observations lead us to the belief that it and the "hydrate of sabadilline" of Couerbe are nondescript mixtures of alteration-products of the other bases present, which we find to be—

(*a.*) The veratrine of Couerbe (amorphous, giving crystalline salts).

(*b.*) The veratrine of Merck (crystallisable; salts non-crystalline, saving the gold salt).

(*c.*) The third base, almost insoluble in ether just referred to (amorphous; salts amorphous).

Of these three bases the first furnishes on saponification dimethyl-protocatechuic (veratric) acid, whilst the second, and apparently also the third gives rise to an acid which is apparently the "cevadic acid" of Pelletier and Caventou (obtained by them from sabadilla seeds, by treating with ether and saponifying the oil thus obtained by potash, *vide* § 3), and also identical with the methyl-crotonic acid of Frankland and Duppa. Accordingly we propose to designate the bodies respectively—

(*a.*) Veratrine (because the prior right to that name rests with this base, and because it furnishes veratric acid).

(*b.*) Cevadine (because it forms cevadic acid).

(*c.*) Cevadilline (because it appears to form cevadic acid, and because in insolubility in ether it corresponds with the "sabadilline" of Weigelin and Dragendorff, which, however, we have been unable to find.

As regards the views of Weigelin, and of Schmidt and Köppen, that the mass of the sabadilla alkaloïd is made up of uncrystallisable bodies, isomeric with "veratria" (of Merck, our cevadine), one of which is soluble in water, our experiments show that the facts observed by them admit of a different explanation. Very small quantities of non-crystalline impurity prevent the "veratrine" of Merck from crystallising readily, whilst a mixture of a non-crystalline salt of Merck's "veratrine" with one of Couerbe's veratrine prevents the latter from crystallising; so that it is impossible to get either the one free base or the other salt to crystallise from such mixtures. On the other hand these alkaloïds readily saponify, especially in contact with alkalis; the supposed soluble modification of "veratrine" is probably simply a salt or mixture of salts formed by partial saponification during standing, &c. (*vide* § 6).

The data from which these conclusions are drawn are given in detail in the subsequent sections.

§ 2. *Isolation of Alkaloïds from Sabadilla Seeds.*

In order to avoid as far as possible saponification during extraction, we employed the process found to give satisfactory results with the aconitine alkaloïds, viz., percolation of the coarsely pulverised seeds with alcohol acidulated with tartaric acid (1 part acid to 100 parts of

seeds), evaporation to a small bulk, precipitation of resin by water, and extraction of alkaloïds by adding sodium carbonate, and repeatedly shaking with ether, the ethereal solution being agitated with tartaric acid to remove alkaloïds, and used over again; in this way a tartaric acid solution of bases free from resin is obtained. Former experimenters have almost invariably extracted the alkaloïds by methods involving heating in contact with dilute sulphuric acid, or with alkalis, or with both successively, which must necessarily have brought about a good deal of saponification; probably, indeed, the veratric acid found by Merck in sabadilla seeds was thus formed. The acid tartrates obtained were then treated with sodium carbonate, and shaken with a moderately large bulk of ether, whereby all was dissolved; the almost colourless ethereal solution obtained utterly refused to crystallise on spontaneous evaporation, nor could any crystals be obtained by dissolving the residue in alcohol, and leaving the solution at rest. On boiling with benzoline the viscid, honey-like mass left, a portion dissolved, which appeared to crystallise indistinctly on spontaneous evaporation; the ethereal solution was therefore cautiously mixed with benzoline (previously diluted with a little ether, to avoid much precipitation), until a permanent precipitate began to form, and set aside; the ether, being more volatile than the benzoline, evaporated most quickly, so that the liquid became relatively richer and richer in benzoline; at first viscid, honey-like masses separated, but when about $\frac{5}{6}$ths of the total alkaloïd had deposited, crystals began to form, and continued to deposit until the end. The crystals, mixed with viscid matter, were stirred up with a few drops of alcohol, and well drained and slightly washed with alcohol on the filter-pump; the nearly pure crystals thus obtained were readily crystallisable from hot alcohol on cooling and standing; after two or three recrystallisations they melted at 205°, and were evidently the alkaloïd described by Merck, and by Schmidt and Köppen, as "veratrine," *i.e.*, the base which, as above stated, we propose to term *cevadine*. On saponification these crystals yielded only cevadic acid; the viscid, honey-like precipitates, however, yielded veratric acid on saponification, with a larger quantity of cevadic acid.

In order to isolate the second base thus evidently present, we endeavoured to crystallise out as much as possible of the cevadine by repeating the evaporation with ether-benzoline; on dissolving up in ether the viscid masses for this purpose, a portion refused to dissolve (the amount of ether used being very much less than in the case of the first ethereal solution). The insoluble portion was purified by solution in tartaric acid, addition of sodium carbonate, and agitation of the freshly precipitated flakes with ether, this process being repeated two or three times. The insoluble substance finally obtained was then examined, as described in § 5; that it was not the base yielding vera-

tric acid on saponification was readily shown, no veratric acid, but instead, cevadic acid being obtained from it on saponification.

The ethereal solution, on treatment with benzoline and evaporation, yielded viscid, honey-like precipitates at first, with finally a small quantity of crystals of cevadine; the only way by which the base yielding veratric acid could be extracted was the following:—The resinoïd precipitates which first separated from the ether-benzoline fluid were dissolved in dilute sulphuric acid, precipitated with ammonia, drained on the filter-pump, and partially dried by exposure to air. On stirring up in a mortar the nearly dry base with dilute nitric acid, a sticky mass of nitrate was formed, of which part was only sparingly soluble in water, even on boiling; the portion insoluble gradually became granular; this was filtered off hot, and purified by two or three boilings with small quantities of water. On regenerating the free base by shaking with sodium carbonate and ether, it was found impossible to crystallise it from ether or alcohol; on saponification it yielded veratric acid copiously; on solution of the base in dilute sulphuric acid, fine crystals of sulphate resembling paper-pulp formed on standing. These were collected and drained on the filter-pump; on drying by spontaneous exposure to air the mass lost its crystalline texture, and became a resinoïd substance of conchoidal fracture; on solution of this in water and standing, crystals were again formed. From the purified crystals of sulphate the base, the *veratrine* of Couerbe, was obtained and examined, as described in § 4.

In the hope of obtaining the "sabadilline" and "sabatrine" of Weigelin, the original liquors from which all alkaloïds soluble in ether had been removed by repeated shaking with that solvent, were agitated with fusel oil, and the fusel oil extract thus obtained was evaporated to dryness. A small quantity of brown resinoïd alkaloïdal matter was thus obtained, which however yielded scarcely a trace to boiling water, and though soluble in ether, benzene, and alcohol, utterly refused to crystallise from any solvent. No appreciable amount of "sabadilline" could therefore have been present in these liquors, Weigelin's method of extracting the body examined by him consisting of agitation of the liquors from which precipitable bases had been thrown down by ammonia with fusel oil, separation of "sabadilline" from "sabatrine" in the fusel oil residue by ether, in which the former is almost insoluble, and purification of the former by solution in water, and crystallisation from benzene.

In this way we obtained from 20 lbs. of sabadilla seeds some 60—70 grams of rough mixture of alkaloïds, finally yielding some 8—9 grams of pure crystallised cevadine; about 5—6 grams of not quite pure veratrine, and 2—3 of rough cevadilline. The great majority of the alkaloïd would not crystallise, nor could crystallisable salts be ob-

tained from it: on analysis and saponification it yielded numbers indicating that it was essentially a mixture of cevadine and veratrine, the former predominating. It is possible, as supposed by Weigelin, and by Schmidt and Köppen, that the substance contained an isomeric modification of cevadine; but it seems far more probable that it was simply a mixture of bases, the one preventing the other from crystallising. On treatment with water, the resinoïd masses left by the spontaneous evaporation of alcoholic or ethereal solutions of these mixtures, part dissolved, the solution drying up to a gummy mass on evaporation; the soluble portion, however, appeared to be simply a mixture of the salts of the bases with cevadic and veratric acids, formed by spontaneous saponification on standing, &c.

In order to obtain a larger quantity of cevadine, some ounces of commercial so-called "veratria" were purchased from Messrs. Hopkin and Williams. This wholly dissolved in ether, yielding no insoluble cevadilline or "sabadilline"; the ethereal solution treated with benzoline behaved just as that prepared by ourselves; at first resinoïd masses separated, and ultimately crystals of cevadine easily purified by alcohol. The resinoïd masses yielded some veratric acid on saponification; but we did not succeed in isolating any granular nitrate of veratrine from them, there being apparently a much smaller quantity of veratrine here than in the batch worked up by ourselves: probably this was due to difference in mode of preparation, the purchased product having been presumably prepared in the ordinary way, which involves heating with dilute sulphuric acid, precipitation with alkalis, and contact with alkaline fluids, &c., highly conducive to loss by saponification.

§ 3. *Composition and Derivatives of Cevadine* (the "Veratrine" of Merck, and of Schmidt and Köppen).

According to Schmidt and Köppen, the crystallised base melts, when pure, at 205°; the purest crystals we obtained by several recrystallisations melted at 206° (corrected), whilst other specimens fused at 203°, 204—205°, and 205°. In the hope of obtaining greater purity, the purest crystals were converted into gold salt, which was then recrystallised from alcohol, and the crystals, after drying in the air to remove adherent spirit, suspended in water and decomposed by sulphuretted hydrogen: the base regenerated from the resulting hydrochloride by means of sodium carbonate and ether, did not crystallise from alcohol so readily as the original substance, and the crystals, after recrystallisation from alcohol, fused at 204°. In other similar experiments in which the gold salt was suspended in alcohol instead of water, the base finally regenerated and recrystallised from

alcohol fused at 205°. No additional purity therefore seemed to be gained by this treatment, but rather the contrary.

The following numbers were obtained on analysis:

(A.) Purest crystals several times recrystallised from alcohol, obtained from sabadilla seeds by the tartaric acid process, &c., as above described.

0·2825 gram gave 0·6680 CO_2, and 0·2160 H_2O.
0·5900 gram burnt with soda lime gave 0·0975 Pt.

(B.) Alkaloïd regenerated from crystallised gold salt.

0·2770 gram gave 0·6590 CO_2, and 0·2135 H_2O.
0·6390 gram burnt with soda lime neutralised acid equal to 0·01456 nitrogen.

(C.) Base prepared from commercial so-called "veratria" purchased from Hopkin and Williams.

0·2570 gram gave 0·6075 CO_2, and 0·1995 H_2O.

(D.) Specimen C recrystallised twice more from alcohol.

0·3085 gram gave 0·7360 CO_2, and 0·2395 H_2O.

	Calculated.		Found.					Mean.
			A.	B.	C.	D.		
C_{32}.....	384	64·97	64·49	64·88	64·46	65·06		64·72
H_{49}.....	49	8·29	8·50	8·56	8·62	8·62		8·57
N	14	2·37	2·34	2·28	—	—		2·31
O_9	144	24·37	—	—	—	—	by diff.	24·40
$C_{32}H_{49}NO_9$..	591	100·00	—	—	—	—		100·00

The gold salts yielded the following numbers after drying at 100° till constant.

From specimen A. 0·5185 gram gave 0·1085 Au = 20·93 per cent.
B. 0·5000 „ 0·1050 21·00 „
D. 0·3720 „ 0·0790 21·13 „

Mean .... 21·04

Calculated for $C_{32}H_{49}NO_9$, HCl, $AuCl_3$ = 21·08

These numbers agree closely with the formula assigned, and moreover are practically identical with those found by Merck, and by Schmidt and Köppen (with the exception, as pointed out above, of Merck's single N determination).

	Calculated for $C_{32}H_{49}NO_9$.	Merck. Mean of 4 combustions, 1 nitrogen and 4 gold determinations.	Schmidt and Köppen. Mean of 7 combustions, 3 nitrogen and 5 gold determinations.	Wright and Luff. Mean of 4 combustions, 2 nitrogen and 3 gold determinations.
Carbon in base..	64·97	64·81	64·63	64·72
Hydrogen.....	8·29	8·71	8·62	8·57
Nitrogen	2·37	5·50	2·66	2·31
Gold in gold salt	21·08	21·01	21·09	21·04

Merck also determined the percentage of carbon and hydrogen in the gold salt, and of carbon and hydrogen and SO_3 in the sulphate, finding numbers very close to those required for the formula $C_{32}H_{49}NO_9$, as is manifest from the circumstance that he deduced from these numbers the formula, $C_{32}H_{52}N_2O_8$ = molecular weight 592 instead of $C_{32}H_{49}NO_9 = 591$. Schmidt and Köppen similarly determined the carbon and hydrogen in the gold salt, the SO_3 in the sulphate, the HCl in the hydrochloride, and the mercury and chloride in the mercurochloride, in all cases finding numbers closely accordant with the formula, $C_{32}H_{49}NO_9$, they themselves deducing from these numbers the almost identical formula, $C_{32}H_{50}NO_9$ = molecular weight 592 instead of 591.

There can, therefore, be no doubt that the formula, $C_{32}H_{49}NO_9$, represents the composition of cevadine as nearly as repeated analysis can possibly fix it: whence it results that the substance examined by Weigelin and Dragendorff, and regarded by them as Merck's base, must have been very impure, for they found the melting point to be 150°, and obtained the percentages—

Carbon in base.....	64·42
Hydrogen in base	8·70
Nitrogen by soda lime	2·92, 2·95, 2·86
,, by volume	2·87
Gold in gold salt.....	23·17, 23·08

hence their formula, $C_{52}H_{86}N_2O_{15}$, *à priori* not very probable, is clearly utt rly erroneous.

Cevadine crystallises anhydrous from alcohol, but from ether it separates only as a varnish, becoming crystalline on moistening with alcohol containing a little water, and well stirring. As previously stated by Merck, and by Schmidt and Köppen, it utterly refuses to form crystallisable salts, with the exception of the aurochloride. On adding gold chloride to a solution of the pure base in hydrochloric acid, an amorphous, very sparingly soluble, yellow precipitate falls, soon becoming crystalline: when drained and boiled with alcohol con-

taining a little water, it dissolves, crystallising in well defined small needles on cooling. The crystals thus obtained contain $C_{32}H_{49}NO_9$. $HCl.AuCl_3 + 2H_2O$, the water of crystallisation being lost at 100° only slowly.

1·4295 grams of air dry crystals lost at 100°
0·0555 gram, becoming constant in weight only after several hours ..... = 3·88 per cent.
Calculated ..... = 3·73 „

Cevadine is powerfully sternutatory; the crystals at first are transparent, becoming white and opaque by exposure to air without material loss of weight.

When cevadine is heated in sealed tubes with water, or better if saponified by cohobation with alcoholic soda, it breaks up in accordance with the reaction—

$$C_{32}H_{49}NO_9 + H_2O = C_5H_8O_2 + C_{27}H_{43}NO_8,$$

perfectly parallel with that undergone by the aconite alkaloïds, and like them forming an acid, cevadic acid, and a new base. The latter, to which we propose to apply the term *cevine*, is non-crystalline, and readily decomposed by long boiling with alkalis, forming a resinoïd non-basic or feebly basic body: wherefore the determination of the amount of acid formed by titration methods is inexact, and the yield of the basic saponification-product but small after purification. The former product (cevadic acid) also appears to be affected by continued boiling with potash, splitting up into propionic and acetic acids to some extent, in just the same way as is effected more rapidly by fusion with potash (*vide infra*): for on acidulating the product of saponification with sulphuric acid, and distilling with a large bulk of water, somewhat more than one equivalent of volatile acid is produced for one of cevadine employed. The acid, $C_5H_8O_2$, thus first produced, corresponds pretty closely with the description of cevadic acid given by Couerbe, and appears to be also identical with the methylcrotonic acid of Frankland and Duppa. To procure it in a pure state, cevadine was saponified by long continued boiling with alcoholic soda, an inverted condenser being attached; the alcoholic fluid was diluted with water, acidulated with sulphuric acid, and distilled as long as any acid came over. A portion of the distillate heated with a slight excess of pure baryta, freed from the excess by a current of carbon dioxide, boiled to a small bulk, filtered, and evaporated to dryness at 100°, yielded a gummy readily soluble residue which did not crystallise on moistening with water and allowing to stand: of this 0·4275 gram gave 0·3075 $BaSO_4$ = 42·29 per cent. Ba.

The formula $Ba(C_5H_7O_2)_2$, requires 40·89 per cent. Ba, whilst barium propionate requires 48·41 per cent., and barium acetate 53·72 per cent., from which it would seem that the production of propionic and acetic acids by secondary action of the alkali is but slight, although quite perceptible both by the process of titration and by the examination of the barium salt.

The acid distillate was neutralised with soda and evaporated to a small bulk; on adding phosphoric or sulphuric acid and heating, a distillate was obtained partly consisting of fluid acids readily soluble in water, and partly of crystals or of an oil becoming crystalline on standing. In another experiment the soda salt was acidulated with sulphuric acid, and shaken with ether; on distillation, after the ether had passed over, an acid liquid began to distil at a little above 100°, the temperature quickly rising, so that the greater part passed over at 185—190°; the distillate at this temperature solidified on cooling to a mass of crystals wetted with an acid liquid. After pressure in blotting paper, pearly scales were obtained, the fusing points of two specimens of which were respectively 64° and 65° (corrected), somewhat lower temperatures being found with less pure specimens. (Methyl crotonic acid melts at 62° (Frankland and Duppa), its isomeride, angelic acid, at 45°.) The acid thus obtained possessed a peculiar aromatic odour somewhat recalling that of butyric acid, but more pleasant: when rendered just neutral with ammonia, silver nitrate threw down a white precipitate somewhat soluble on washing; the silver salt thus formed darkened slightly on drying in the dark; another specimen prepared by boiling the acid with freshly precipitated well washed silver carbonate, filtering hot, and leaving the filtrate to evaporate spontaneously over sulphuric acid in the dark, consisted of perfectly white granular crystals, which yielded the following numbers:

First crop of crystals, 0·4285 gram gave 0·4570 CO_2, 0·1365 H_2O, and left behind 0·2235 gram Ag.

Second crop obtained on further evaporation, 0·3005 gram gave 0·1575 Ag.

	Calculated.			Found.	
				1st crop.	2nd crop.
C_5	60	28·99		29·08	—
H_7	7	3·38		3·54	—
Ag.....	108	52·17		52·16	52·41
O_2	32	15·46	(by diff.)	15·22	—
$C_5H_7O_2.Ag$..	207	100·00		100·00	

The copper salt of this acid, prepared by precipitating the neutral barium salt with copper nitrate, was so far soluble in water as to be readily dissolved during washing—

0·0790 gram dried over sulphuric acid gave 0·0245 CuO = 31·0 per cent.

The formula Cu $(C_5H_7O_2)_2$, requires = 30·4 per cent.

On heating to 100° the copper-salt was apparently decomposed, as it gave off a strong odour of the acid, and lost in weight nearly 4 per cent.

On fusion of a known weight of acid with caustic potash at about 280° hydrogen was evolved; on dissolving the product in water, neutralising exactly, and then adding enough standard acid to set free about 5 per cent. of the total acids present, no crystallisable substance was extracted by agitation with ether, indicating complete decomposition. Enough acid was then added to set free about 15 per cent. of the acids formed, and the whole distilled until scarcely any more acid passed over; the distillate, on agitation with pure barium carbonate, evaporation to a small bulk, filtration, and evaporation to dryness, yielded a varnish-like salt, of which

0·2520 gram gave 0·2080 $BaSO_4$ Ba = 48·52 per cent.
Calculated for Ba $(C_3H_5O_2)_2$.... = 48·41 „

Enough acid to liberate all acid present, save some 20 to 30 per cent., was then added, and the whole distilled; the barium-salt from this distillate contained 50·61 per cent. Ba, indicating a mixture of propionate and acetate; finally, the last portions of acid were liberated, distilled off, and made into barium-salt: of this, when dried at 100°—

0·1705 gram gave 0·1545 $BaSO_4$ Ba = 53·27 per cent.
Calculated for Ba $(C_2H_3O_2)_2$ .. = 53·72 „

Hence, on fusion with potash the acid saponification-product of cevadine splits up into propionic and acetic acids with evolution of hydrogen, thus: $C_5H_8O_2 + 2H_2O = C_3H_6O_2 + C_2H_4O_2 + H_2$, in this respect exactly agreeing with both angelic and methyl crotonic acids. As, however, the former melts at 45° and the latter at 62° (Frankland and Duppa), whilst our specimens melt at 64° and 65° respectively, there can be little doubt that our acid is actually methyl-crotonic acid.

The cevadic acid obtained by Pelletier and Caventou appears to have been this saponification product in an imperfectly pure state; they do not appear to have separated the crystallised acid completely from other substances (*e.g.*, the propionic and acetic acids formed by its partial decomposition), and hence found that it melted at 20°; in all other respects their description of cevadic acid exactly tallies with our product (which, when not freed from small quantities of fluid acids, melts in the hand): in particular the ammonium-salt of our product yields with ferric chloride the white, or nearly white, floccu-

lent precipitate, described by Pelletier and Caventou as similarly formed with their cevadic acid. Moreover, it is highly probable that Pelletier and Caventou's substance was actually formed by the decomposition of cevadine, for they obtained it by treating the seeds with ether (probably containing alcohol), and saponifying the resinous matter extracted with potash; were any alkaloïd or alkaloïdal salt dissolved out along with the resinous matter, it must inevitably have given rise to our acid by this treatment.

Hence, as there remains little doubt that "cevadic acid" is really identical with the saponification-product of cevadine, and as this name is of earlier date than "methyl-crotonic acid," we propose to keep to the former term in referring to this acid.

In order to isolate the complementary alkaloïdal product *cevine*, the acid liquid left after distilling off the volatile acid was filtered from resinous matter, rendered alkaline with caustic soda, and shaken with fusel oil; the filtered fusel oil extract left on evaporation a brownish varnish, which dissolved in dilute acetic acid, leaving behind resinous flakes. The filtrate from these, on treatment with soda and fusel-oil (after fractionally precipitating to get rid of colouring matter) gave an amber-coloured varnish perfectly soluble in acids; in a capillary tube this did not frit below 140°, and fused at 145°; in alcohol and fusel-oil it dissolved readily, in chloroform but sparingly, in ether hardly perceptibly. Neither the base nor its salts were obtained crystallised. On analysis the following numbers were obtained:—

0·2650 gram gave 0·6215 CO_2 and 0·2035 H_2O.

0·7255 gram burnt with soda-lime, and titrated gave 0·02038 nitrogen; by conversion into platinum-salt gave 0·1400 Pt.

	Calculated.		Found.	
C_{27}	324	63·65	63·96	—
H_{43}	43	8·45	8·52	—
N	14	2·75	2·81	2·73
O_8	128	25·15		
$C_{27}H_{43}NO_8$..	509	100·00		

By adding potassium mercuriodide to a solution of cevine in acetic acid white flakes were precipitated insoluble in water, or nearly so; after drying over sulphuric acid, and finally at 100°—

0·4920 gram gave 0·3210 AgI Iodine = 35·24 per cent.
Calculated for $C_{27}H_{43}NO_8.HI.HgI_2$.... = 34·94 „

It results from these experiments that the formula of cevadine may be written—

$$(C_{27}H_{42}NO_7)—O—CO—C(CH_3)=C_2H_4,$$

since on saponification it forms methyl-crotonic acid, known to have the structure, $C_2H_4{=}C(CH_3) - CO.OH$. In order to see if cevadine is analogous to the aconite alkaloïds in containing hydroxyl-groups also, the base was heated to 100° with twice its weight of benzoic anhydride (containing a trace of fluid impurity which rendered it liquid at 100°) for three hours. On dissolving the product in a little alcohol, adding ether and aqueous tartaric acid, and shaking, an aqueous acid solution of tartrates was obtained; from this, by the aid of caustic soda and ether, the alkaloïds were withdrawn. On spontaneous evaporation the ethereal solution deposited fine arborescent crystals half an inch in length on the side of the dish (cevadine does not crystallise from ether), with only a very small quantity of non-crystalline matter; by stirring up the residue with a little ether, filter-pumping, and slightly washing with ether, the new derivative was obtained snow-white. The crystals when air dry were hydrated, containing $C_{39}H_{53}NO_{10}1\frac{1}{2}H_2O$, the base itself being formed by the reaction—

$$C_{32}H_{49}NO_9 + (C_7H_5O)_2O = C_7H_6O + C_{32}H_{48}(C_7H_5O)NO_9,$$

and hence being *benzoyl-cevadine*. It fused at a temperature between 170° and 180°, the melting point not being clearly defined, and the substance beginning to frit together at 160°—

0·5425 gram dried in the air lost at 100° 0·0205 = 3·78 per cent.

0·4805 gram dried over sulphuric acid lost at 100° 0·0180 = 3·75 per cent.

Calculated = 3·74 per cent.

0·2760 gram dried at 100° gave 0·6780 CO_2 and 0·2050 H_2O.

	Calculated.		Found.
C_{39}	468	67·34	67·00
H_{63}	53	7·63	8·25
N.....	14	2·02	
O_{10}	160	23·02	
$C_{32}H_{48}(C_7H_5O)NO_9$..	695	100·00	

0·3005 gram of gold-salt dried at 100° gave 0·0565 Au = 18·80 per cent.

Calculated for $C_{39}H_{53}NO_{10}.HCl.AuCl_3$ = 18·95 per cent.

Hence it results that cevadine contains one and only one hydroxyl-group, so that its formula may be written—

$$(C_{27}H_{41}NO_6)<\begin{matrix}OH\\O.CO.C(CH_3){=}C_2H_4.\end{matrix}$$

On comparing this formula with that deduced for pseudaconitine (this Journal, 1878, i, 151),

$$(C_{27}H_{37}NO_5)\begin{cases}OH\\OH\\OH\\O.CO.C_6H_9(O.CH_3)_2,\end{cases}$$

it is noticeable that the carbon in the two nitrogenous radicles is the same, whilst the other elements are not very far apart; so that it is highly probable that some deeper connection exists between these two alkaloïds than mere similarity in structure, so far as saponifiability and presence of hydroxyl-groups are concerned. The results described in the next section indicate that veratrine (of Couerbe) is closely allied to cevadine, being indicated by the formula $(C_{28}H_{44}NO_7)-O.CO.C_6H_3(O.CH_3)_2$, and possibly by $(C_{28}H_{43}NO_6)<^{OH}_{O.CO.C_6H_3(OCH_3)_2}$, whilst aconitine contains a radicle with C_{26}, being indicated by the formula $(C_{26}H_{35}NO_7\begin{cases}OH\\OH\\OH\\O.CO.C_6H_5\end{cases}$; so that it is also highly probable that the sabadilla and aconite bases generally are allied together, having perhaps some common central nucleus-radicle.

§ 4. *Composition and Derivatives of Veratrine (the Veratrine of Couerbe).*

The following numbers were obtained with the base isolated as described in § 2, from the crystals of the sulphate by treatment with sodium carbonate and ether, and spontaneous evaporation; no crystals could be obtained from the varnish-like residue by the use of any solvent tried, or by any artifice—

0·2440 gram dried at 100° gave 0·5805 CO_2 and 0·1755 H_2O.
0·2455 „ „ 0·5755 „ 0·1790 „
0·8310 gram burnt with soda-lime gave by titration 0·01681 nitrogen, and by conversion into platinum-salt 0·1320 Pt.

	Calculated.		Found.		Mean.
C_{37}.....	444	64·63	64·88	63·93	64·41
H_{53}	53	7·71	7·99	8·09	8·04
N	14	2·04	2·02	2·24	2·13
O_{11}.....	176	25·62			
$C_{37}H_{53}NO_{11}$.	687	100·00			

0·4590 gram of gold-salt gave 0·0885 Au ..... = 19·28 per cent.
0·5035 „ „ 0·0960 „ ..... = 19·07 „
Calculated for $C_{37}H_{53}NO_{11},HCl.AuCl_3$..... = 19·10 „

The gold-salt was wholly non-crystalline; on adding gold chloride to a solution of the base in hydrochloric acid a gelatinous yellow precipitate was thrown down, drying to a semi-translucent horny mass over sulphuric acid, and not crystallisable from alcohol. On triturating the alkaloïd with dilute nitric acid a horny nitrate was produced, almost insoluble in water, even when boiling; dilute sulphuric acid readily dissolved the base, the solution crystallising in extremely fine needles on standing; on drying, these needles adhered and finally became a horny translucent mass, reproducing crystals on solution in water and standing. The hydrochloride exhibited a similar behaviour, save that the crystals were not so well marked and distinct. It was hoped that a check on the formula deduced from the above numbers might be obtained from the analysis of the crystals of sulphate prepared by dissolving the base in a slight excess of sulphuric acid, draining the crystals formed on the filter-pump, and recrystallising from water; the horny mass into which the crystals ultimately passed on exposure to air gave the following numbers:—

0·5000 gram of air-dry substance (constant in weight in the air) lost at 100° 0·0945 gram = 18·90 per cent.

0·4055 gram of the dry residue gave 0·1000 $BaSO_4$: H_2SO_4 = 10·36 per cent.

The acid sulphate, $C_{37}H_{53}NO_{11}.H_2SO_4$, requires H_2SO_4 = 12·48 per cent.

The neutral sulphate $(C_{37}H_{53}NO_{11})_2\ H_2SO_4$ requires H_2SO_4 = 6·66 per cent., whence it results that the recrystallised salt was a mixture of neutral and acid sulphates, the latter predominating; the formula,

$$C_{37}H_{53}NO_{11}.H_2SO_4.10H_2O,$$

would require 18·65 per cent. of water of crystallisation.

In a capillary tube veratrine fuses at 180° (corrected). Couerbe states that his product fused at 115°, but doubtless his substance was far from pure, not having been regenerated from a crystallised salt.

On saponification with alcoholic soda veratrine breaks up in accordance with the reaction—

$$C_{37}H_{53}NO_{11} + H_2O = C_9H_{10}O_4 + C_{28}H_{45}NO_8,$$

forming veratric acid (dimethyl protocatechuic acid), and a base so closely resembling cevine in its properties that the two might well be regarded as identical were not somewhat different numbers given on combustion. To call to mind that this new base is related to veratrine somewhat as aconine to aconitine, pseudaconine to pseudaconi-

tine, and cevine to cevadine, we propose to term it *verine*. Like cevine, it is to a great extent decomposed by the alkali used in its production, forming a resinous product insoluble in dilute acids.

1·235 grams of veratrin yielded, by treatment with ether, an extract consisting of veratric acid with a little yellowish resinous matter. On titration by standard soda the acid corresponded to 0·344 $C_9H_{10}O_4$.

1·535 grams corresponded similarly to 0·426 $C_9H_{10}O_4$.

	Calculated.	Found.	
Veratric acid formed.....	26·5	27·8	27·7

The slight excess found is probably due, as in the case of the aconite alkaloïds, to the feeble acidity of the resinous bye-product.

The veratric acid thus obtained was purified by dissolving in ammonia, digestion with animal charcoal, and precipitation by hydrochloric acid. After crystallisation from boiling water, anhydrous crystals were obtained, melting at 176—178° (corrected), and giving the following numbers on combustion:—

0·2565 gram gave 0·5595 CO_2 and 0·1355 H_2O.

	Calculated.		Found.
C_9	108	59·34	59·49
H_{10}	10	5·49	5·86
O_4	64	35·17	
$C_9H_{10}O_4$..	182	100·00	

On fusion with caustic potash it formed protocatechuic acid in quantity, readily identified by its colour reaction.

To obtain the complementary product, verine, the liquid from which the veratric acid had been removed by ether was rendered alkaline by soda and repeatedly shaken with fusel oil. On evaporation over the water-bath a brownish-yellow amorphous base was left, which was purified by solution in acetic acid, filtration from a few resinous flakes, and regeneration by means of soda and fusel oil. After drying at 100°, an amber-coloured varnish was obtained, yielding the following numbers:—

0·2705 gram gave 0·6405 CO_2 and 0·2160 H_2O.

	Calculated.		Found.
C_{28}.....	336	64·25	64·57
H_{45}	45	8·60	8·87
N	14	2·68	
O_8	128	24·47	
$C_{28}H_{45}NO_8$..	523	100·00	

Neither verine nor any of its salts appeared to be crystallisable. In

all its properties it resembled cevine most closely, save in melting point. In a capillary tube it fritted at 95° (as it also did in the water-bath). On raising the temperature it gradually became a thick viscid mass, exhibiting no distinct melting point, and not becoming completely fluid till heated to about 130°, whilst cevine exhibited no signs of fritting below 140°, and completely fused at 145°.

From these results it is evident that veratrine possesses a composition analogous to that of cevadine, its formula being—

$$(C_{28}H_{44}NO_7) - O.CO.C_6H_3(O.CH_3)_2.$$

The amount of material at our disposal was too small to enable us to examine the action of benzoic anhydride on veratrine, and to decide how many (if any) hydroxyl groups are present; and for this reason we were unable to multiply analyses, and especially to form and examine crystallised salts. It may, therefore, perhaps happen that further experiments may cause the formula attributed to this alkaloïd to be slightly altered, the analytical numbers above stated being not incompatible with other formulæ differing but little from $C_{37}H_{53}NO_{11}$, although this formula agrees best with the numbers found. It is noticeable that the formula $C_{36}H_{51}NO_{11}$ would represent veratrine and cevadine as possessing a common radicle when these formulæ are written—

$(C_{27}H_{42}NO_7) - O.CO.C_6H_3(O.CH_3)_2$ and $(C_{27}H_{42}NO_7) - O.CO.C_4H_7$,

and would also indicate cevine and verine as being identical. That this is the case, however, is rendered improbable, not only by the difference in analytical numbers found with these two decomposition-products, but also by the difference in their melting points. Both of these differences, however, might possibly be due to a slight impurity in one of the specimens.

§ 5. *Composition and Derivatives of Cevadilline.*

In the hope of obtaining the substance described by Weigelin as "sabadilline," for comparison with the body isolated by us, and to which we propose to apply the term cevadilline (§ 1), a substance was purchased from Messrs. Burgoyne, Burbidges, Cyriax, and Farries, under the name of "sabadilline." On examination this proved to contain no trace of any substance possessing the properties of Weigelin's product, but instead to be almost wholly composed of a base identical with our cevadilline.

The crude cevadilline obtained as described in § 1, and the material purchased from Messrs. Burgoyne and Co., were each purified in the following way. The substance was dissolved in tartaric acid, precipitated with sodium carbonate, and shaken repeatedly with ether.

From the purchased product scarcely anything was dissolved out, and that little appeared to be identical with the undissolved portion; from our material ether dissolved only traces after the first two or three treatments with that solvent, these traces being apparently identical with the undissolved flakes. The insoluble substances were then shaken with cold benzene, which in each case dissolved out only minute quantities, the benzene extracts yielding no crystals on spontaneous evaporation, but only small quantities of varnish, apparently identical with the undissolved portions. Water too dissolved out next to nothing from either substance; whence manifestly Weigelin's "sabadilline" was not present in either our preparation or the substance bought under the name of "sabadilline."

The substances finally obtained consisted of amorphous flakes soluble in boiling benzene, and separating out in amorphous flakes on cooling, readily soluble in fusel oil. The fusel oil solutions left, on evaporation, dark amber resins, which were purified by treating with acetic acid, filtration from a little undissolved matter, and finally regeneration by means of soda and fusel oil. The varnishes thus obtained much resembled verine and cevine; on analysis they yielded practically identical numbers, agreeing fairly with the formula $C_{34}H_{53}NO_8$.

A. Base prepared by ourselves from sabadilla seeds—
0·2445 gram gave 0·6020 CO_2 and 0·2020 H_2O.

B. Base prepared from purchased product—
0·2375 gram gave 0·5885 CO_2 and 0·2005 H_2O.

0·7405 gram with soda lime gave by titration 0·01602 nitrogen; by Pt salt, 0·1120 Pt.

	Calculated.		Found.	
C_{34}.....	408	67·66	67·14	67·57
H_{53}	53	8·79	9·16	9·37
N	14	2·32	—	2·17 2·14
O_8.....	128	21·23		
$C_{34}H_{53}NO_8$..	603	100·00		

On solution in acetic acid and addition of mercuriodide of potassium, white semigelatinous precipitates were obtained in each case, which on drying over sulphuric acid became horny and semi-transparent, after drying at 100°,

Specimen A. 0·4720 gram gave 0·2765 AgI, I = 31·65 per cent.
„ B. 0·6905 „ 0·4120 „ I = 32·24 „
Calculated for $C_{34}H_{53}NO_8$, HI, HgI_2 ..... I = 32·15 „

Gold chloride threw down in each case semi-gelatinous non-crystallisable precipitates. That from B yielded the following numbers:—

0·3860 dried over sulphuric acid for some weeks gave 0·0810 Au, Au = 20·98 per cent.

Calculated for $C_{34}H_{53}NO_8,HCl,AuCl_3$ = 20·81 per cent.

At 100° this appeared to decompose, darkening much in colour, and losing in weight several per cents.

On saponification with alcoholic soda, each specimen gave rise to a volatile acid, apparently identical with the cevadic acid obtainable from cevadine, no trace of veratric acid being formed. As with cevadine, the acid distilled over on acidification with sulphuric acid of the saponified product slightly exceeded one equivalent for one of alkaloïd employed. The quantities of material at our disposal were too small for complete study of this reaction. Admitting, as is highly probable, that the same kind of saponification takes place with cevadilline as with cevadine and veratrine, and that cevadic acid is formed, the reaction would be—

$$C_{34}H_{53}NO_8 + H_2O = C_5H_8O_2 + C_{29}H_{47}NO_7.$$

Should this be substantiated on further examination, the alkaloïdal saponification-product might be termed *cevillin*, bearing to cevadilline exactly the same relationship as cevine to cevadine, *i.e.*, differing by $+ H_2O$ − cevadic acid.

§ 6. *Constitution of Uncrystallisable Bases from Sabadilla Seeds.*

On saponifying with alcoholic potash the viscid bases precipitated on spontaneous evaporation of the ether benzoline solutions described in § 1, similar results were obtained, both with the substances prepared by ourselves, and those similarly obtained from the alkaloïdal mixture purchased from Messrs. Hopkin and Williams. In each case both veratric and cevadic acids were formed, in such quantities as to show that these non-crystallisable substances were wholly, or almost wholly made up of saponifiable bases: for the total acid formed (which distilled off after acidulation with sulphuric acid, and that extracted by ether) neutralised somewhat more standard soda than corresponded with the alkaloïd used, the excess probably arising from decomposition of the cevadic acid into propionic and acetic acids. The veratric acid thus produced neutralised in each case much less soda than the volatile acid, indicating a considerable preponderance of the base which yielded cevadic acid, viz., cevadine. On combustion of the amorphous base prepared by the tartaric process numbers were obtained agreeing fairly with a mixture of cevadine and veratrine, the former predominating;

precisely similar results were obtained with the alkaloïdal products of the saponification of the amorphous bases, isolated by means of soda and fusel oil, and purified, as described above in § 3—

0·2670 gram of amorphous base yielded 0·6370 CO_2 and 0·2025 H_2O.
0·4040 „ gold-salt gave 0·0820 Au.

	Calculated. For veratrine.	For cevadine.	Found.
Carbon in base....	64·63	64·97	65·07
Hydrogen.....	7·99	8·29	8·43
Gold in gold salt..	19·10	21·08	20·29

0·1395 gram of mixed verine and cevine formed by saponification gave 0·3240 CO_2 and 0·1090 H_2O.

Calculated. For Verine.	For Cevine.	Found.
64·41	63·65	63·34
8·04	8·45	8·67

On treating with water, after standing for some weeks, the soft non-crystalline masses which separated from the ether benzoline, as described in § 2, a portion dissolved; the solution of this dried up to a gum, and yielded precipitates with alkalis. That this was not a soluble modification of cevadine, as supposed by Weigelin, and by Schmidt and Köppen, but only a mixture of salts formed by partial saponification was shown by the fact that on distillation with water, after slight acidulation with sulphuric acid, cevadic acid passed over.

On the whole, therefore, it appears that the supposed isomeric modifications of "veratrine" (cevadine) are only either mixtures of bases, preventing each other from crystallising, or alteration-products.

§ 7. *General Conclusions.*

From the foregoing experiments, conjoined with the results detailed in the papers of former investigators, we draw the following conclusions:—

(1.) The seeds of *Veratrum Sabadilla* (sometimes designated *Veratrum officinale*, *Sabadilla officinarum*, or *Asagræa officinalis*) contain an alkaloïd, first isolated by Couerbe, and termed by him *veratrine*, which is indicated by the formula, $C_{37}H_{53}NO_{11}$, or one very close thereto; this is non-crystalline, but furnishes certain crystallisable salts: on saponification it splits up into veratric acid (dimethyl-protocatechuic acid) and a new base, *verine*, thus—

$$C_{37}H_{53}NO_{11} + H_2O = C_9H_{10}O_4 + C_{28}H_{45}NO_8.$$

(2.) In addition, a considerably larger quantity of another alkaloïd

is present, first isolated by Merck, and described by him as "veratrine." To distinguish this from the former alkaloïd, which has the prior claim to the name veratrine, we propose to term it *cevadine*, reserving the name veratrine for Couerbe's base. This cevadine is crystallisable, melts at 205—206°, and on saponification splits up in accordance with the reaction—

$$C_{32}H_{49}NO_9 + H_2O = C_5H_8O_2 + C_{27}H_{43}NO_8,$$

forming a base *cevine*, and an acid identical with the methyl-crotonic acid of Frankland and Duppa, and with the cevadic acid of Pelletier and Caventou.

(3.) The formulæ assigned by Merck, by Weigelin, and by Schmidt and Köppen, to cevadine are all more or less erroneous, that of the latter pair of chemists being nearest to the truth, $C_{32}H_{49}NO_9$.

(4.) There is no good reason for supposing the existence of isomeric modifications of cevadine (so-called "veratrine") in the sabadilla alkaloïds, these supposed bodies being either mixtures of bases, thereby rendered highly difficult to crystallise, or products of alteration by saponification of the above-named bases.

(5.) The body described as "sabadilline" by Weigelin was not to be found in the substances examined by us; neither in the alkaloïds extracted by ourselves by the tartaric acid process; nor in the commercial so-called "veratria" obtained from Hopkin and Williams; nor in the product purchased as "sabadilline" from Burgoyne and Burbidges. On the other hand, the first and last of these substances contained an alkaloïd almost insoluble in ether, and agreeing in that respect with "sabadilline," but non-crystalline and insoluble in water, and differing therefore in these respects; this body gave numbers agreeing with $C_{34}H_{53}NO_8$, and on saponification appeared to form cevadic acid. To indicate this latter fact and to connote its partial resemblance to "sabadilline," we propose to term it *cevadilline*.

(6.) The "sabatrine" of Weigelin is doubtless simply a mixture of resinoïd alteration-products, as is also Couerbe's "hydrate of "sabadilline."

(7.) The sabadilla alkaloïds are not merely constituted like the aconite bases (*i.e.*, as regards saponification, and, in the case of cevadine, hydroxylation), but they also contain nitrogenous radicles, which appear to be closely allied to those of the aconite alkaloïds.

XLII. *On the Action of Oxides on Salts.* Part I.

By Edmund J. Mills, D.Sc., F.R.S., "Young" Professor of Technical Chemistry in Anderson's College, Glasgow, and David Wilson.

1. The action of oxides on salts leads in general to the formation of other oxides, derived from the salts in question. Our experiments have had for their object the determination of the law whereby this result is attained. They may not improbably throw some light on the general theory of the decomposition of salts; and we believe that they may be of practical interest in connection with certain technical processes, of which the manufacture of glass is not the least important.

In the present paper we refer only to the action of tungstic, silicic, and titanic oxides on potassic carbonate at a high temperature. That action is attended with the formation of new alkaline salts, and the evolution of carbonic dioxide; owing to the latter circumstance it exhibits the remarkable property of being incapable of simultaneous inversion.

2. The experiments were carried out as follows. A quantity of purified oxide under examination was weighed into a platinum crucible of 14 cub. centims. capacity, and a nearly constant amount (5·3206 grams) of anhydrous purified potassic carbonate then added.

The weight of carbonate was always taken so very near to the standard weight, that the results could afterwards be easily reduced to that standard.

The platinum crucible was placed inside a larger one, from which it was separated by a few fibres of asbestos; and, the larger one having been covered with its lid, the whole arrangement was placed in a gas-furnace, where it was heated for a definite interval of time.

3. The loss of weight on ignition consists of carbonic dioxide, and is a measure of the chemical effect of the masses in action. A slight correction has, however, to be applied to this loss, inasmuch as the carbonate itself loses weight during ignition. This correction was readily attained as follows. If WO_3 be represented by a weight of about ·25 gram, then it is found by experiment that WO_3 expels CO_2 (within the usual range of error) + ·010 gram. We have therefore deducted ·010 gram from every such determination of carbonic dioxide. As an additional guarantee of the accuracy of our work, we ascertained in the experiments with tungstic oxide, the amount of residual carbonate by means of an ordinary carbonic acid apparatus, and found

the loss thence calculated to agree well with the results of direct estimation.

4. In stating the numerical results, we shall always refer the actual weights to ordinary chemical units, or, as we shall term them for shortness' sake, "units." These units are the quotients, $\frac{\text{actual weight}}{\text{symbolic value}}$; thus 5·3206 grams of potassic carbonate represent—

$$\frac{5{\cdot}3206}{K_2CO_3} = \frac{5{\cdot}3206}{138{\cdot}14} = {\cdot}0385160 \text{ unit.}$$

The following values will be employed in this paper:—

$$CO_2 = 43{\cdot}92,\ K_2CO_3 = 138{\cdot}14,\ WO_3 = 231{\cdot}93,\ SiO_2 = 59{\cdot}92,\ TiO_2 = 32{\cdot}12.$$

I. *Tungstic Oxide.*

5. This oxide is readily attacked by potassic carbonate, forming a mixture which fuses at a comparatively low temperature. By means of a calorimeter designed after Weinhold by Mr. Wm. Thorp, B.Sc. (to whom we were indebted for the instrument), and employing the method based upon the specific heat of wrought iron, we found the temperature to be approximately 750° C. The duration of each operation was one hour. In the following table, ϵ represents the chemical effect, or units of carbonic dioxide evolved, when m units of tungstic oxide are taken; both values being reduced to a uniform number (·038516) of units of carbonate.

TABLE I.

m.	ϵ Found.	ϵ Calculated.	Diff. per Cent.
·0010758	·001076	—	—
·0021567	·002167	·0021486	−0·85
·0087811	·008737	·0087355	−0·01
·0169896	·016463	·016693	+1·40
·0301884	·029367	·029439	+0·25
·0345135	·033823	·037769	−0·16
·0345039	·033843	·033785	−0·17
·0366391	·035316	·035280	−0·10
·0387996	·037568	·037446	−0·32
·0431535	·038554	—	—
			Sum +0·04

6. If N represent the constant number of units of carbonate, and $n = \epsilon$, the units of carbonic dioxide evolved, $(N - n)$ will represent the number R remaining unattacked after the reaction; for every

unit of carbonate corresponds exactly with a unit of carbonic dioxide. The experimental numbers, then, suggest the following relation:—

$$(m - n) = \tau\left\{\frac{m}{N - n}\right\} = \tau\left\{\frac{m}{R}\right\},$$

τ being a constant. Hence

$$n = \frac{m(\tau - N)}{(n - N) - m},$$

which obviously may be reduced to

$$n = \frac{\alpha \,.\, m \,.\, N}{(N - n) + m}, \text{ or } \epsilon = \frac{\alpha m N}{R + m} \qquad (1).$$

In this equation, α represents the fraction of a unit of carbonate that is decomposed by a unit of tungstic oxide; it is a constant of chemical condition, depending on the total circumstances which, throughout this set of experiments, have influence on the chemical effect. Rejecting the first experiment on account of its having been used to determine the carbonate's loss by ignition, and the last experiment because it makes the value of n slightly higher than is possible, the remaining eight relations give $\alpha = \cdot99597$, with a probable error of $\cdot00152$. We have thus the equation—

$$\epsilon = \frac{\cdot99597(\cdot038516m)}{(\cdot038516 - n) + m},$$

to the course of the reaction. It is graphically represented by a hyperbola with an oblique asymptote.

II. *Silicic Oxide.*

7. The silica employed was prepared by passing silicic fluoride into ammonia-water, and igniting the precipitate. It was, on the whole, not so readily attacked by potassic carbonate as was tungstic oxide. We heated the mixture for a quarter of an hour to about 750° C., and then for three-quarters of an hour to about 880°.* If the operation were commenced at the latter temperature, it was liable to be lost by intumescence. We shall assume that two silicates are present from the first, and write the equation to the reaction as follows:

$$\epsilon = \frac{(\alpha + \beta m)Nm}{R + m} = \frac{(\cdot82237 + \cdot21319m)(\cdot038516m)}{R + m},$$

which represents a hyperbola with oblique asymptotes.

* According to Carnelley (*Chem. Soc. J.*, 1876, i, 505), potassic carbonate melts at 838°.

TABLE II.

m.	ϵ Found.	ϵ Calculated.	Diff. per Cent.
*·016689	·012001	·012288	+2·39
·016699	·011864	·012254	+3·29
·025043	·017635	·017392	−1·38
·033381	·020718	·020838	+0·58
*·033381	·021426	·021131	−1·38
·041720	·025722	·024503	−4·74
·050056	·026100	·025709	−1·50
·066772	·028467	·028007	−1·61
*·100140	·028869	·029641	+2·67
			Sum 1·68

The value of α and β have been calculated, as well by the case subsequently, by the method of least squares. The probable error of nine determinations of $(\alpha + \beta m)$ is ·0048649, or 0·58 per cent. on the mean value (·83377). Since $(\alpha + \beta m)$ cannot exceed 1, the maximum value of m is ·83320; or $\frac{\cdot 83320}{\cdot 038516} = 21{\cdot}63 SiO_2$ at most would be required, under the conditions, to expel CO_2. The minimum active ratio is SiO_2 : ·82237 K_2CO_3, or approximately, 6 SiO_2 : 5 K_2CO_3 (for which α = ·83). The extremes of composition in known potassic silicates are $\frac{1}{2}SiO_2 : K_2O$ and 24 $SiO_2 : K_2O$.

8. Some reference must here be made to the labours of previous experimenters. Rose† in 1821, confirming a previous result of Berzelius, found that SiO_2 gives rise to the evolution of CO_2, *i.e.*, unit for unit. He did not, however, regard his results as exact.

Yorke (*Phil. Trans.*, 1857, 535), taking somewhat varied quantities of silica and potassic carbonate, found as a mean of four determinations a ratio which we have corrected to SiO_2 : ·994 CO_2. His operations were carried on in a crucible heated over "a gas-flame urged by bellows,"—at a much higher temperature therefore than ours. Bloxam (*Chem. Soc. J.*, 1859, xii, 197) also, proceeding in the same manner as Yorke, obtained the (corrected) ratio SiO_2 : ·935 CO_2.

9. A more extensive set of experiments was carried out by Scheerer (*Ann. Chem. Pharm.*, 1860, cxvi, 152—154). According to this investigator, there is considerable evidence to show that the least action of potassic carbonate upon silica leads to the formation of the salt K_2SiO_3; the extreme action—*i.e.*, at a high temperature, with excess

* A specially dense sample of silica, prepared in the same manner as the other, but strongly ignited for several hours.

† *Ann. Chem. Phys.*, xxiii, 362—3.

of the carbonate—to the salt K_4SiO_4. His determinations were made with a constant amount of silica, the amount of carbonate being variable. If M = ·75 = silica taken, n = carbonate employed, and ϵ = the chemical effect at a red heat (all in modern units*), we have—

$$\epsilon = \frac{(\alpha + \beta n)\,\mathrm{M}n}{\mathrm{R} + m} = \frac{(\cdot 91748 + \cdot 0087849n)\cdot 75n}{\mathrm{R} + \cdot 75}.$$

TABLE III.

n.	ϵ Found.	ϵ Calculated.	Diff. per Cent.
0·50	0·46	0·44	−4·4
0·75	0·57	0·56	−1·8
1·50	0·61	0·64	+4·9
3·00	0·67	0·69	+3·0
4·50	0·71	0·71	0·0
25·00	0·86	0·86	0·0
			Sum +2·7

The probable error of six determinations of $(\alpha + \beta n)$ is 0·84 per cent. on the mean value (·96910). It appears, then, that at a red heat, which exceeds the temperature at which we worked, the salt first formed is principally dipotassic, but that this gradually becomes mixed with an amount of tetrapotassic salt which increases as more carbonate is added. In this case 9·39 K_2CO_3 correspond to ·75 CO_2 per ·75 SiO_2, which is in the ratio 12·52 K_2CO_3 : CO_2 : SiO_2. When n is very small, the ratio is ·91748 SiO_2 : K_2CO_3, or 1·09 K_2CO_3 : 1·09 CO_2 : SiO_2.

10. The following is a reduction of Scheerer's experiments performed at a bright red heat (*gelbgluth*). The equation is—

$$\epsilon = \frac{(\alpha + \beta n)\,\mathrm{M}n}{\mathrm{R} + m} = \frac{(\cdot 97832 + \cdot 012306n)\cdot 75n}{\mathrm{R} + \cdot 75}.$$

TABLE IV.

n.	ϵ Found.	ϵ Calculated.	Diff. per Cent.
0·50	0·50	0·49	−2·0
0·75	0·62	0·63	+1·6
1·00	0·67	0·69	+3·0
1·50	0·74	0·74	0·0
3·00	0·78	0·77	−1·2
4·50	0·80	0·78	−2·5
25·00	0·97	0·97	0·0
			Sum −1·1

* Scheerer does not give weights.

The probable error of the seven determinations of $(\alpha + \beta n)$ is ·0045346, or 0·44 per cent. on the mean value. Putting $\alpha + \beta n = 1$, $n = 1{\cdot}7617$, whence the ratio $SiO_2 : CO_2 \frac{1{\cdot}7617}{{\cdot}75} K_2CO_3$, or $SiO_2 : CO_2 : 2{\cdot}35\, K_2CO_3$.

11. The factor (β) for producing polypotassic salt has increased with the temperature, and the results as a whole are more regular. It is indeed very probable that they are as regular as the temperature. We have therefore in this reaction a chemical pyrometer of not inconsiderable value for furnace heats. To establish it, all that would be necessary would be to tabulate values of $(\alpha + \beta m)$ or $(\alpha + \beta n)$ against known temperatures. Two crucibles, with different weights of silica and carbonate in each, would suffice for a single determination. Or the temperature might be measured directly by weighing the carbonic dioxide expelled.

12. The difficulty of completely decomposing potassic carbonate by means of silica is obviously one of the chief reasons why, in the manufacture of glass with the help of these materials, the temperature requires to be so high and the silica in considerable excess; and because even these conditions are inadequate to the purpose, metallic oxides, such as lime or minium, are brought to their aid.

III. *Titanic Oxide.*

13. The action of titanic oxide on potassic carbonate is much more sluggish than that of silica on the same salt. This may perhaps in part be explained by Rose's observation (*loc. cit.*), that the potassic titanate formed has a great tendency to settle to the bottom of the crucible. Our experiments were consequently of longer duration and more intense in their nature, the temperature being approximately 880° and the time three hours. The results are as follows:—

$$\epsilon = \frac{({\cdot}71917 + 3{\cdot}6813m)\,({\cdot}038516m)}{R + m}.$$

TABLE V.

m.	ϵ Found.	ϵ Calculated.	Diff. per Cent.
·0060796	·0046034	·0043409	−5·68
·012170	·009093	·0086097	−5·32
·018276	·011541	·012234	+6·00
·024367	·014437	·015670	+8·50
·036517	·022472	·022842	+1·65
·048716	·029486	·029195	−0·99
·060890	·035059	·034381	−1·93
·073084	·038128	·037861	−0·93
			Sum +1·41

The probable error of eight determinations of $(\alpha + \beta m)$ is 1 per cent. nearly, on the mean value. Putting $\cdot71917 + 3\cdot6813\, m = 1$, a maximum, $m = \cdot076286$; hence the ratio $\frac{\cdot076286}{\cdot038516}$ $TiO_2 : CO_2$, or 1·98 $TiO_2 : CO_2$. It appears, then, that complete decarbonation is effected when the reagents are nearly in the proportion to form dititanate.

Summary of Results.

14. The experimental results are comprised in the following table:—

TABLE VI.

Oxide.	Condition.	Units of Oxide required to expel CO_2 from K_2CO_3.	Units of Carbonate required to yield CO_2.
Tungstic	750°	∞	—
Silicic	880°	21·63	—
„	Red heat.	—	12·52
„	Bright heat.	—	2·35
Titanic	880°	1·98	—

15. The numbers of units of oxide required to expel CO_2, *i.e.*, to produce the unit of chemical effect, have been calculated from expressions of the form—

$$\epsilon = \frac{\phi mn}{R + m}; \qquad (2).$$

where ϵ represents the chemical effect, m and n represent units of oxide and carbonate (one of which only has been made variable), R is the undecomposed residue of carbonate, and ϕ is a linear function of the variable. When ϕ is expressed by a number, it may be termed the "factor of condition." So far as our work at present extends, ϕ involves one constant only when a single salt is formed and two constants when two are formed. The deduced values of ϕ are but little influenced by moderate experimental errors,—a fortunate circumstance in researches of this nature where the conditions are very difficult to control.

In the case of titanic oxide only do we find anything like a close approximation to the simple integral values required by ordinary chemical equations. Here the relation,—

$$K_2CO_3 + 2TiO_2 = K_2O.2TiO_2 + CO_2,$$

is very nearly borne out by a maximum value of ϕ in one of our sets

of experiments. We have not, however, been able to elicit any trustworthy evidence for

$$K_2CO_3 + WO_3 = K_2O.WO_3 + CO_2,$$
$$K_2CO_3 + SiO_2 = K_2O.SiO_2 + CO_2,$$
$$\text{or } 2K_2CO_3 + SiO_2 = 2K_2O.SiO_2 + 2CO_2.$$

16. According to equation (2) the chemical effect of an oxide and a carbonate, acting on one another under the conditions we have specified, is directly proportional to the product of their active masses, and inversely proportional to the sum of their residues. It is intended by further inquiry to ascertain how far these simple relations admit of extension.

17. Equation (2) is evidently a special instance of one more general. For it is clear that the typical equation must contain the chemical effect as unity and the factor of condition as unity, without indicating change of weight. We have thus $\epsilon = 1$, $\phi = 1$; and $R = n$, say; whence

$$1 = \frac{mn}{n + m}$$
$$\text{or } n + m = mn \qquad (3).$$

This is a mere transliteration of Brodie's fundamental chemical equation,

$$x + y = xy.$$

It may be inferred, then, that *Brodie's fundamental equation represents the mutual action of two bodies under unit conditions, apart from change of weight, and with the unit of chemical effect.*

XLIII.—*Action of Hydrochloric Acid upon Various Metallic Salts.*

By J. W. Thomas.

In a former paper (*Chem. Soc. J.*, xxxiii, 72) reference was made to the absorption of hydrochloric acid gas, and to some compounds capable of neutralising hydrochloric acid in solution.

The experiments which I carried out were of three kinds:—1. Compounds were introduced into tubes containing hydrochloric acid gas standing over mercury. 2. A current of hydrochloric acid was passed over compounds placed in a glass tube, one end of which was connected with a flask containing strong sulphuric acid (to dry the gas) and the other end was joined to a bottle containing water for the purpose

of absorbing the excess of hydrochloric acid, or, as in some instances, the tube had a long neck which dipped under mercury so that the gases might be collected. 3. Compounds were dissolved in water, and different proportions of hydrochloric acid added and then distilled over a water-bath at 100°, or in a vacuum at 30°, or at the ordinary temperature of the laboratory (about 15°). If the compound was to be passed up into a tube over mercury, it was first ground into fine powder and then slightly moistened if anhydrous, and afterwards wrapped tightly in a piece of filter-paper (so as to obtain a porous agglomerated mass) and dried as thoroughly as the nature of the substance would allow. Those compounds which lose their water of crystallisation only at high temperatures were dried in an air-bath or over a lamp in platinum dishes. In two experiments the compounds were dried by heat or over sulphuric acid, according to their character.

Compounds introduced into tubes containing Hydrochloric Acid Gas standing over Mercury.

Potassic nitrate (dry) absorbs the gas very rapidly, the mercury rising and filling the tube in about a minute; the mercury soon lowers, however, as nitrate of mercury is formed and nitric oxide is evolved.

Sodic nitrate and *ammonic nitrate* behave in a similar manner, but the latter compound absorbs the gas less quickly.

The neutral *oxalates of potassium*, *sodium*, and *ammonium* absorb hydrochloric acid gas with great facility, but oxalate of calcium does not.

Oxalate of lead, and *oxalate of barium* made by precipitating chloride of barium with ammonium chloride, absorb the gas very quickly.

Neutral tartrates of sodium and *potassium* absorb the gas very slowly when in a hard caky condition, somewhat rapidly when porous. *Tartrate of ammonia* absorbs the gas quickly. *Rochelle salt* (dry) is a good absorbent for hydrochloric acid gas. When the hydrous salt, which fuses rapidly, is made into a ball on the end of a platinum wire and passed up into a tube of the gas, the latter is quickly absorbed at first, but the absorption proceeds much more slowly after a few minutes. *Potassio-antimonic tartrate* absorbs the gas very rapidly, but the tartrates of lead and magnesium do not.

Neutral citrates of sodium and *potassium* absorb hydrochloric acid gas somewhat rapidly. *Diammonic citrate* behaves in a similar manner.

Citrate of lead absorbs the gas very quickly, the salt turns brown, and the surface of the mercury is attacked.

Crystals of ammonia and potash-alum, sulphate of zinc, and sulphate of magnesium absorb hydrochloric acid by virtue of their water of crystallisation, but the anhydrous salts do not absorb the gas.

Ferrocyanide of potassium, in crystals or anhydrous, absorbs the gas very rapidly, but ferricyanide of potassium does not.

Dry Hydrochloric acid passed over Compounds in a glass tube.

When the gas was passed over *nitrate of ammonium* in dry powder it was rapidly absorbed and drops of water condensed on the inside of the tube. A little chlorine and nitric oxide were given off, but not until the experiment had lasted some time. There was no apparent rise in temperature, in fact it seemed to lower. Ammonium chloride was formed.

Dry hydrochloric acid passed over *nitrate of potassium* in dry powder gave rise to a very energetic action. Water condensed on the inside of the tube very rapidly and chloronitric gas was given off. Nitrous fumes in the tube indicated the production of nitrous acid, and in a short time the salt became a pasty mass. The heat evolved was intense and the quantity of chlorine and nitric oxide very considerable. The nature of the action is dependent upon the volume of dry hydrochloric acid which is made to pass through the tube, and when that volume is large, chloronitric gas is given off copiously. Potassium chloride is formed.

Nitrate of sodium was next tried and used in a dry and granular condition. The action was very similar to that upon potassium nitrate; dense brown vapours were formed when the gas evolved came in contact with the atmosphere, and much chlorine was given off. The temperature rose considerably, but not so high as in the previous experiment. Sodium chloride is formed.

Nitrate of aluminium, dried over sulphuric acid, was subjected to a current of dry hydrochloric acid for some time, but it was not acted upon.

Dry hydrochloric acid passed over *nitrate of bismuth* gives rise to a very energetic action; water is formed, large volumes of chlorine and nitric oxide are disengaged, and possibly oxides of chlorine and other nitrogen oxides are generated. The reaction is an exceedingly complex one, and in consequence of mercury being violently attacked by the gaseous products, it was useless to collect them over it. No satisfactory result attended the collection of the products over water. The heat evolved during the reaction was very considerable. Chloride of bismuth was formed.

Nitrate of barium is not attacked by dry hydrochloric acid.

Nitrate of cadmium (dry) is attacked with great energy by hydro-

University of Michigan

chloric acid; the temperature rises very high, water is formed, and clouds of chlorine and nitric oxide are evolved. The hydrous nitrate ($CdN_2O_6.4OH_2$) is also decomposed and chloride of cadmium is formed.

Nitrate of calcium is not altered by dry hydrochloric acid.

When dry hydrochloric acid was passed over *nitrate of cobalt* (dried over sulphuric acid) the effect was instantaneous and very beautiful; the pink colour changed to blue in the bulk, and emerald-green towards the outer edges. Much water was soon formed and the pink colour returned. The action was very energetic; chloronitric gas was evolved and the temperature rose considerably. The salt with its 6 atoms of water is similarly but less violently attacked. Chloride of cobalt is formed.

Nitrate of copper (dried over sulphuric acid) is rapidly decomposed by dry hydrochloric acid; the compound soon becomes pasty and there is a copious evolution of gas. Nitrous fumes appear in the tube, and there is much chlorine and nitric oxide given off and apparently some nitrogen. The temperature rises high. The hydrous salt ($CuN_2O_6,3OH_2$) is similarly acted upon and cupric chloride is formed.

Nitrate of lead is violently attacked by dry hydrochloric acid. Water is formed and a large volume of chloronitric gas is evolved the instant the action commences. Nitrous fumes appeared at the beginning of the experiment, which were partly due to the nitric oxide combining with the oxygen of the air in the tube. Chloride of lead is formed.

Nitrate of lithium is acted upon slowly by dry hydrochloric acid; very little heat is evolved, and the quantity of chlorine and nitric oxide given off is not great.

Nitrate of magnesium, dried over sulphuric acid until it lost two-thirds of its water of crystallisation, was readily decomposed by dry hydrochloric acid. Water and nitrous acid were formed, and chlorine and nitric oxide were evolved. The temperature rose appreciably. Chloride of magnesium was formed.

Nitrate of manganese, dried over sulphuric acid, is acted upon by dry hydrochloric acid, manganic chloride and hydrate and water are formed, and chlorine and nitric oxide are given off. The salt liquefies, forming a dark-brown solution which deposits a large quantity of manganic hydrate when water is added. The hydrous salt, $MnN_2O_6,6OH_2$, is decomposed in a similar manner.

Mercuric, mercurous, and mercuroso-mercuric nitrates are all violently attacked by dry hydrochloric acid. Mercurous and mercuric chloride and water are formed, and chlorine and nitric oxide are evolved. The heat generated is considerable.

Nitrate of nickel. This compound turns yellowish-green when dry hydrochloric acid is passed over it, and an energetic action commences. The temperature rises appreciably, and chlorine and nitric oxide are given off. Chloride of nickel is formed.

Nitrate of silver is so quickly converted into chloride of silver by dry hydrochloric acid, that there is very little chlorine or nitric oxide evolved. Nitric acid and chloride of silver are the chief products.

Nitrate of strontium is not decomposed by dry hydrochloric acid.

Nitrate of uranium, with rather less than half of its water of crystallisation was used. It was rapidly acted upon by dry hydrochloric acid, with formation of much heat, and oxychloride of uranium and water were formed, and chlorine and nitric oxide were evolved.

Nitrate of zinc, with about 4 atoms of water of crystallisation, was attacked with great energy by dry hydrochloric acid. Nitrous acid, chloride of zinc, and water were formed, and chlorine and nitric oxide generated. The temperature did not rise considerably.

Owing to the fact that chlorine, free and in combination with nitric oxide as chloronitric gas, is evolved generally in large quantity when dry hydrochloric acid acts upon nitrates, there is great difficulty attached to the determination of the nature of the gaseous products, as they cannot be collected over mercury or water without suffering decomposition.

Dry hydrochloric acid passed over *bichromate of potassium*, determines the separation of chromic acid, the salt assuming a beautiful crimson colour. The chromic acid set free is afterwards reduced, and the substance turns brown, and then consists of water, chromic chloride, and the brown oxides of chromium mixed with potassium chloride —no chlorochromic acid is formed. The temperature rises appreciably.

Chromate of potassium is decomposed by dry hydrochloric acid, which forms potassium chloride, water, and bichromate of potassium in the first part of the reaction, and subsequently the bichromate is reduced in the same manner as before recorded.

Biborate of sodium (anhydrous) is not attacked by dry hydrochloric acid.

Citrate of potassium ($C_6H_5K_3O_7,H_2O$) was subjected to the action of dry hydrochloric acid. The dipotassic anhydrous salt was first formed, and water, vapourised by the heat evolved, was condensed on the inside of the tube. Subsequently monopotassic citrate was formed, and the water was again absorbed. There is no appreciable heat generated during the latter part of the reaction. Two-thirds of the potassium is converted into chloride, but the citric acid is not attacked.

Dry hydrochloric acid acted violently on *citrate of lead*—empyreu-

matic vapours were disengaged during the first part of the experiment, and the citric acid was decomposed, and appeared as if it were charred. Much water was soon deposited in the tube, and the further decomposition of citric acid was arrested. Chloride of lead was formed. The temperature rose high.

Metantimonate of potassium is readily attacked by dry hydrochloric acid, the chlorides of antimony and potassium and water are formed, and chlorine is disengaged. The reaction is energetic, and considerable heat is generated.

Potassio-antimonic tartrate, dried at 100°, was subjected to the action of dry hydrochloric acid. The compound was rendered pasty through the formation of water, and acid tartrate of potassium and chloride of antimony were the resulting products.

Dry hydrochloric acid passed over *chlorate of potassium* caused clouds of euchlorine to be evolved, and water was formed.

Hypochlorite of sodium (dry) is violently attacked by dry hydrochloric acid; a large volume of hypochlorous acid and chlorine is given off, and water is formed by the action of hydrochloric acid upon the liberated hypochlorous acid. Sodium chloride is the resulting compound. There is a considerable rise in temperature.

Bisulphate of sodium is readily decomposed by dry hydrochloric acid, sodium chloride, water, and sulphur dioxide are formed. *Thiosulphate of sodium* is also decomposed with facility, free sulphur, sulphur dioxide, water, and sodium chloride being the resulting products.

Dry hydrochloric acid, passed over *ferrocyanide of potassium*, gave rise to much heat, and potassic chloride and ferroprussic acid were formed.

Permanganate of potassium is violently attacked by dry hydrochloric acid. Clouds of chlorine are disengaged, and water, potassium chloride, manganic hydrate, and manganous, and probably manganic chloride, are the first products of the reaction. The temperature rises considerably.

Molybdate of ammonium is attacked by dry hydrochloric acid, and much heat is generated. Water, ammonium chloride, and molybdic trioxide are formed, together with a little dioxide of molybdenum, and a corresponding quantity of chlorine is given off.

Dry hydrochloric acid, passed over *dry ammonium, sodium, or potassium sulphates* is absorbed, and one-half of the base is converted into chloride.

Action of Hydrochloric Acid upon Sulphates of Alkali in Solution.

In the experiments referred to on p. 77 of this volume, the following methods were adopted in order to ascertain if hydrochloric acid formed

acid sulphate of ammonia and ammonium chloride when added to a saturated aqueous solution of the neutral sulphate of ammonium. Equal volumes of a saturated (16°) solution of sulphate of ammonium and the hydrochloric acid solution, B, mentioned in the paper referred to, were mixed together and introduced into a flask which was connected by a bent tube (passing through the cork of the flask) with an intermediate vessel joined to a Sprengel pump. A vacuum was formed and the volatile contents of the flask were distilled over into the intermediate vessel which contained a little nitrate of silver solution, for the purpose of indicating hydrochloric acid if it passed over. The flask was heated to 30°, and, after a considerable time, the residue crystallised out and appeared quite dry, while the nitrate of silver in the distillate was not in the least turbid. A similar result was obtained when sodium sulphate was substituted for ammonium sulphate. These experiments, together with those which follow relating to hydrochloric acid converting neutral sulphates of alkali into acid sulphates, led me to conclude, as stated at p. 77 of this volume, that the free hydrochloric acid in a solution of cuprous chloride was neutralised by a saturated aqueous solution of either ammonium or sodium sulphate. From recent experiments I found that in consequence of having a long tube forming the neck of the flask which contained the cuprous chloride and ammonium sulphate solutions, some of the water in the act of distilling over (*in vacuo*) condensed in the tube passing through the stopper of the flask and ran back; and on account of the affinity of hydrochloric acid for water, no acid passed over into the receiving vessel. This state of things continued until the contents of the flask partly crystallised out and acid sulphate was formed. I have since used a similar form of apparatus, and placed pure strong sulphuric acid mixed with about 5 c.c. of a saturated aqueous solution of sulphate of silver in the intermediate bottle.

It is unnecessary to enter further into detail respecting the numerous experiments carried out, but the results showed that when a moderately dilute hydrochloric acid solution of cuprous chloride is added to a saturated solution of ammonium or sodium sulphate, the hydrochloric acid is stable by reason of its being so diluted, but it is not neutralised. At the ordinary temperature of the atmosphere, hydrochloric acid does not appear to convert the neutral alkali sulphates in solution into acid sulphates, but at about 40° it does. If only a small quantity of hydrochloric acid is added to an aqueous solution of an alkali sulphate containing six times the equivalent of base, the solution may be evaporated without loss of hydrochloric acid.

Sulphate of sodium was boiled with water containing more hydrochloric acid than was equivalent to the total sodium and concentrated, so that when the solution was cooled down to the temperature of the

room, a little salt would crystallise out. Small well-defined crystals of sodium chloride separated unmixed with any sulphate. By again concentrating the solution, more crystals of sodium chloride were obtained, and by repeating the treatment, the greater portion of half the sodium crystallised out as sodium chloride almost free from acid sulphate. Sulphate of sodium boiled with excess of hydrochloric acid (dilute) until the solution was saturated at the boiling temperature deposited on cooling a mixture of acid sulphate of sodium and sodium chloride, but the first portion which crystallised out contained the most sodium chloride. *Sulphate of ammonium* was next tried, and similar results were obtained; ammonium chloride crystallised out first, and when *sulphate of potassium* was used, potassium chloride crystallised out first; so that the action of hydrochloric acid on sulphates of alkali in a hot solution determines the formation of acid sulphate and chloride of alkali, and the latter being insoluble in the solution containing acid sulphate, crystallises out first. *Sulphate of lithium* (neutral) is not converted into acid sulphate by hydrochloric acid.

Action of Hydrochloric Acid on Phosphates of Alkali.

Tribasic phosphates of potassium, sodium, and ammonium, and the phosphate of sodium and ammonium were separately dissolved in water, and hydrochloric acid added equal to $\frac{2}{3}$ the equivalent of the base, and the solution subjected to distillation in a vacuum. The distillates were all neutral. Further experiments were tried with these compounds, but since making them I notice that Stolba (*Zeitschr. Anal. Chem.*, xvi, 100) has devised a method for estimating the phosphoric acid in ammonio-magnesic phosphate, volumetrically, by means of hydrochloric acid which combines with two atoms of the base. He found that alkali phosphates are acted upon in a similar manner.

Action of Hydrochloric Acid on Oxalates, Citrates, and Tartrates of Alkali in Solution.

The neutral oxalates of sodium, ammonium, and potassium were separately dissolved in water, and hydrochloric acid equivalent to half the base added, and the solution distilled over a water-bath. All the distillates were neutral. When more acid was added than was equivalent to half the base, the distillate was invariably acid (HCl).

The tribasic citrates of potassium and sodium were dissolved in water, hydrochloric acid equivalent to two-thirds of the base was added, and the solution distilled into sulphuric acid in a vacuum. No hydrochloric acid distilled over. Diammonic citrate with hydrochloric acid equivalent to half the ammonia was dissolved in water and distilled in

a vacuum—the distillate was free from hydrochloric acid. When the hydrochloric acid added to the solution of alkali citrates exceeded the above proportions, the distillates were always acid (HCl).

Aqueous solutions of the neutral tartrates of ammonium, sodium, and potassium were mixed with hydrochloric acid equal to half the base, and distilled over a water-bath. The distillates were all neutral. When mixed with a larger quantity of hydrochloric acid the distillates were acid (HCl). Hydrochloric acid added to Rochelle salt precipitates acid tartrate of potassium; acetic, oxalic, citric, nitric, and sulphuric acids act likewise.

XLIV.—*On the Chemical Aspect of Vegetable Physiology.*

[A Lecture delivered before the Chemical Society, May 3rd, 1878.]

By Sydney H. Vines, B.A., F.L.S., Fellow of Christ's College, Cambridge.

The investigation of the various substances which compose the tissues and which are contained in the cells of plants, has been for a long time zealously pursued by chemists, and the study of the decompositions which they undergo under the action of various reagents has afforded results which have contributed largely to the philosophy of chemistry. In fact it may be said that Organic Chemistry owes its existence to the numerous researches which have been made in this direction. And yet, strange to say, comparatively few attempts have been made to discover the significance of these substances in the economy of the plant. In discussing the subject which we have to consider this evening, I will attempt to lay before you as clearly as possible some at least of the conclusions arrived at on this point by the combined efforts of chemists and physiologists.

I will begin with the consideration of a substance which occurs in the majority of plants—chlorophyll. This substance plays an essential part in the performance of a function which is characteristic of green plants, and is perhaps the most important of all physiological functions—the function of "assimilation," which consists in the absorption of carbonic anhydride from the air; in its decomposition in the chlorophyll-corpuscles, with evolution of oxygen; and in the formation of starch-grains in the chlorophyll-corpuscles by the combination of the retained carbon with the elements of water. The history of the discovery of this function, and of the gradually in-

creasing appreciation of its importance, is of great interest, but time will not allow me to do more than to sketch it very briefly.

De la Hire,* and, after him, Bonnet,† found that green plants, or parts of plants, immersed in water and exposed to sunlight gave off bubbles of gas; and Bonnet further observed that no bubbles were given off if the water had been previously boiled. Priestly‡ pointed out that the air evolved by leaves under these circumstances was "dephlogisticated," and Ingenhouss§ showed that this evolution of gas is due, not to the warmth of the sun, but chiefly, if not only, to its light. Sénébier‖ insisted upon the importance of "fixed air" (CO_2) in the process, and proved that the amount of "pure air" evolved by green plants in water is greater when a considerable amount of "fixed air" is held in solution. De Saussure¶ observed that the volume of the oxygen exhaled was less than that of the carbonic anhydride absorbed, and that the decomposition of carbonic anhydride by green plants is accompanied by an increase in their weight.

At the beginning of the present century the sum total of knowledge upon this subject amounted to this, that green parts of plants, when exposed to sunlight, decompose the carbonic anhydride contained in the air, evolving a volume of oxygen which is less than that of the absorbed carbonic anhydride, and that at the same time they increase in weight.

For several years no important publication on this subject appeared. In 1837** von Mohl drew attention to the almost universal occurrence of starch-grains in chlorophyll-corpuscles, and especially pointed out that these starch-grains were secondary formations within the corpuscles. These observations were confirmed and extended by Nägeli and Cramer.†† In 1862 Sachs‡‡ showed that starch-grains do not occur in etiolated chlorophyll-corpuscles, and that their formation in normal corpuscles is dependent upon exposure to light.§§ He tacitly

* *Mém. de l'Acad.* 1690.

† *Usage des Feuilles.* 1754.

‡ *Phil. Trans.* 1772.

§ *Experiments on Vegetables.* 1779.

‖ "Expériences sur l'action de la lumière solaire. 1788." Macbride had pointed out as early as 1764, that "fixed air," is absorbed by green plants when exposed to sunlight.

¶ *Recherches Chimiques sur la Végétation.* 1804.

** "Unters. üb. die Anatom. Verhältnisse des Chlorophylls." Reprinted in the *Vermischte Schriften.* 1845.

†† *Pflanzenphysiologische Untersuchungen.* Heft ii. 1858.

‡‡ *Bot. Zeitung.* No. 44. "Ueber den Einfluss des Lichts auf die Bildung des Amylums in den Chlorophyllkörnern." See also *Bot. Zeitung.* 1864. No. 38.

§§ Böhm, however, has found that when normal plants are exposed to feeble light the starch disappears from the chlorophyll-corpuscles, but reappears after an in-

assumes, though he gives no facts in proof, that this formation of starch-grains can take place only when the assimilating organ is supplied with carbonic anhydride, an assumption which has since been fully substantiated by Godlewski.* It will be seen at once that the appearance of starch-grains in the chlorophyll-corpuscles and the decomposition of carbonic anhydride, with evolution of oxygen, are dependent upon the same conditions, viz., (1) presence of CO_2 in the air;† (2) presence of chlorophyll; (3) exposure to light. Sachs is therefore justified in concluding that these phenomena belong to the same function, that the formation of starch in the assimilating organ is a consequence of the decomposition of the carbonic anhydride: and in this way the increase of weight observed by De Saussure to take place in plants, which for some time had been actively decomposing carbonic anhydride and evolving oxygen, can be satisfactorily explained.

Hitherto it has been assumed that starch is always the product of assimilation, but this is not a universal rule. In some Monocotyledons (*e.g.*, the onion) no starch can at any time be detected in the chlorophyll-corpuscles, and it appears that in these plants another carbohydrate, glucose, is formed instead. Recently it was stated‡ (Briosi) that oil was produced in certain plants (*Musa* and *Strelitzia*) by assimilation, but the researches of Holle§ and Godlewski§ have shown that this assertion is without foundation. That a carbohydrate is the product of assimilation may be deduced from some of De Saussure's results. He found that the increase of weight observed in some of his experiments amounted to rather more than twice the weight of the carbon contained in the absorbed carbonic anhydride. (In one case the increase in weight was 531 grams, and that of carbon 217 grams.) This proportion nearly corresponds with that which the carbon contained in a carbohydrate bears to the total weight of the carbohydrate ($C_6H_{10}O_5 = 162$ and $C_6 = 72$).

Further, Boussingault‖ determined that the volume of oxygen

terval, which may extend over two or three weeks. Under these circumstances the starch-grains cannot be regarded as products of assimilation; they must have been supplied from the reserve carbohydrates stored up in the plant. This does not, however, alter the fact that the starch-grains which appear in the chlorophyll-corpuscles under ordinary circumstances are produced by assimilation. (See *Sitzungsber. der K. Akad. d. Wissensch. Wien.* Bd. LXIX. 1874. Bd. LXXIII. 1876; and *Ber. d. Deutsch. Chem. Gesellsch. Jahrg.* 10. 1877.)

* *Flora.* 1873.

† See a paper by J. Moll, in the *Landwirthschaftliches Jahrbuch of Nathusius und Thiel.* 1877. "Ueber die Herkunft des Kohlenstoffs der Pflanzen."

‡ *Bot. Zeitung.* 1873.

§ *Flora.* 1877.

‖ *Comptes rendus*, t. liii. 1861.

exhaled by assimilating organs is approximately equal to that of the carbonic anhydride absorbed, a proportion which favours the assumption that a carbohydrate has been formed, according to the following equation:—

$$6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2.$$

We have now to inquire in what way this process takes place; how it is that the chlorophyll-corpuscle is capable of forming starch within it. It is obvious that any satisfactory answer to such an inquiry must be based upon an accurate knowledge of the composition and properties of chlorophyll. Unfortunately we are not at present in possession of such knowledge, although many investigators have endeavoured to attain it. It is not certainly known whether chlorophyll is a definite substance (according to Pringsheim,* Wiesner,† and Karl Kraus‡), or a mixture of one or more blue with one or more yellow constituents (Frémy, Filhol, Stokes, Sorby, Gregor Kraus§). *A priori* the former view would appear to be the more probable, and all the more recent experiments tend to establish it. The supporters of this view give the name of "chlorophyll" to a substance which corresponds generally with the "blue constituents" of chlorophyll according to the latter view; and they regard the "yellow constituents" as being colouring matters which coexist with the chlorophyll, and either give rise to it or are formed from it. This diversity of opinion is doubtless to be attributed to the fact that none of the solvents as yet employed dissolve chlorophyll without more or less decomposing it. For the same reason its ultimate composition is still not accurately determined. The earlier analyses (those of Mulder, Morren and Morot) represent chlorophyll to be a nitrogenous substance. Pfaundler‖ could detect only 0·037 per cent. of nitrogen in it, which he regarded as being due to impurities. Kromayer,¶ however, found 7 per cent. of nitrogen in chlorophyll obtained by extraction of the leaves of the wheat with alcoholic potash, and Timiriaseff** goes so far as to say that chlorophyll contains an ammonia compound, to which he gives the name of *chlorophyllin*. Probably iron also enters into the molecule of chlorophyll, and this probability is reduced almost to a certainty by Wiesner's recent researches.†† All

* *Monatsbericht d. Berl. Akad.*, 1874, p. 628; 1875, p. 745. See also Conrad, *Flora*. 1872.

† *Entstehung des Chlorophylls*, Wien. 1877.

‡ *Flora*. 1875.

§ *Zur Kenntniss der Chlorophyll-farbstoffe*. 1872.

‖ *Liebig's Annalen*, vol. 115.

¶ *Arch. Pharm.*, vol. 156, and *Chem. Centralblatt*, 1861.

** *Bot. Zeitung*. 1869.

†† *Loc. cit.*

these moot points, however, must necessarily remain undecided until a satisfactory solvent for chlorophyll is discovered.

Since our knowledge of the composition of chlorophyll is so incomplete, it is not surprising that its significance in the function of assimilation should have been explained on theories which differ widely. There seems to be a general concurrence in the opinion that the chlorophyll in assimilating organs is constantly undergoing change, but the nature of this change is very variously described. Wiesner* considers that the chlorophyll becomes oxidised, the oxygen being derived from the absorbed carbonic anhydride, and he bases his view upon the fact that an alcoholic solution of chlorophyll becomes oxidised when exposed to light. Without attempting to enter upon a discussion of this view, it may be pointed out that, if this be the case, it is difficult to account for the elimination of oxygen which accompanies assimilation, for Wiesner's own experiments seem to show that the evolution of oxygen and the decomposition of chlorophyll take place simultaneously. It is also not easy to suggest in what way a continuous supply of fresh reducing material (chlorophyll) is kept up.

Another hypothesis has been brought forward by Karl Kraus.† He suggests that chlorophyll is a product of assimilation, for it is formed in consequence of it, and is at the same time the cause of it, for assimilation cannot take place without it; that is to say, that the chlorophyll in process of development, and not the chlorophyll which is already formed, is the cause of assimilation. He considers that chlorophyll is the result of the combination of the products of the decomposition of carbonic anhydride with a substance to which he gives the name of *leucophyll*. The chlorophyll is then decomposed by the rays of light which it absorbs, the leucophyll is set free to combine again with the products of the decomposition of carbonic anhydride, and the formation of starch commences. This hypothesis can hardly be accepted at present as a satisfactory explanation, for it is unsupported by experimental evidence, and it presents obvious difficulties. A third explanation has been offered by Sachsse.‡ He regards chlorophyll as being the first product of the process of assimilation, and considers that under the influence of light it is converted into starch or some substance of the same physiological value. In support of his views he draws attention to the fact that the chlorophyll of the living plant is constantly undergoing decomposition, and he infers that consequently a fresh formation of it is continually taking place. In order to prove a genetic connection between chlorophyll and carbo-

* *Sitz. Ber. d. Wien. Akad. Math.-naturw. Classe*, vol. 69.

† *Loc. cit.*

‡ *Chemie u. Physiologie der Farbstoffe, etc.* 1877.

hydrates, he cites Baeyer's* experiments, in which a colouring matter was synthetically formed (by the action of an aldehyde, furfurol, upon a member of the aromatic group, pyrogallol or resorcin), resembling chlorophyll in some of its chemical and optical properties. Of course this substance is not identical with chlorophyll; but, if it be admitted that it is related to the colouring matters of the chlorophyll group, the mode of its formation indicates a genetic connection between chlorophyll and the carbohydrates. It is known that the carbohydrates can be oxidised to aldehydes, and that under certain circumstances they can be decomposed in such a way that various aromatic substances are produced. It appears, then, from Baeyer's experiments, that it is possible to form a colouring matter allied to chlorophyll by a synthesis of the products of the decomposition of carbohydrates.

The question now arises as to the possibility of the occurrence of such a synthesis in the living plant. It has already been suggested by Baeyer† that the first product of the simultaneous decomposition of carbonic anhydride and of water in assimilating cells is formic aldehyde, according to the formula—

$$CO_2 + H_2O = COH_2 + O_2.$$

Karl Kraus‡ has recently (1875) made some interesting experiments which seem to support this view. He grew maize plants in the dark, and supplied some of them with a dilute solution of methyl alcohol, a substance which is readily oxidised to formic aldehyde. He found that the leaves of the plants growing in the dilute alcohol became distinctly green in the dark, whereas those of the plants grown in pure water were etiolated. It appears, therefore, to be probable that a formation of aldehyde takes place under normal conditions. As to the occurrence of aromatic substance, which is essential to the formation of chlorophyll, there can be no uncertainty. Substances belonging to this group have been found in so many plants that it is not unreasonable to infer that they exist in all. Moreover, the presence of one member of this group, pyrocatechin, first detected in a living plant (*Ampelopsis hederacea*) by von Gorup-Besanez,§ has been demonstrated by Karl Kraus in the growing parts of many plants, more especially of those which contain no tannin. Evidence of another kind is afforded by the observations of Wiesner,‖ of

* *Deut. Chem. Ges Ber.*, v, 1096.
† *Deut. Chem. Ges. Ber.*, iii.
‡ *Loc. cit.*
§ *Sitzungsber. d. phys.-med. Soc. Erlangen.*, 1871 and 1874.
‖ *Jahrb. f. Wiss.* Bd. viii.

Drude,* and of Prillieux,† upon the presence and mode of origin of chlorophyll in parasitic and saprophytic plants, such as *Neottia*, *Nidus-avis*, *Monotropa Hypopitys*, and the *Orobanchaceæ*, and by those of Sachs‡ and Weiss§ upon the coloration of chlorophyll corpuscles. In all these cases the starch present in the cells was seen to diminish in quantity as the amount of colouring matter increased. That a genetic connection exists between carbohydrates and chlorophyll seems therefore to be placed beyond doubt. According to Sachsse's view, the carbohydrates stored up in a seed undergo, at the time of germination, a decomposition, probably of the nature of oxidation, as a result of which aldehyde and aromatic substances are formed, which combine to form a yellow chlorophylloïd colouring matter, *etiolin*. If the seedling be not exposed to light, no further change takes place (except in the case of Ferns and Conifers), but under the influence of light the etiolin is converted into chlorophyll, probably by a process of reduction.

The next question to be considered is, whether chlorophyll is converted into carbohydrates in the process of assimilation, that is, whether it forms part of a cycle of chemical changes, which begins with carbohydrates and goes on, through chlorophyll formed from the products of their decomposition, to the reconstitution of carbohydrates by a reduction of the chlorophyll, or whether chlorophyll simply causes the decomposition of the carbonic anhydride of the air, and thus renders possible a combination of carbon with the elements of water to form carbohydrates.

Sachsse argues that chlorophyll is actually converted into a carbohydrate either by a simple reduction, that is, by a continuation of the reducing process by which chlorophyll is formed from etiolin, or by a re-arrangement of its molecules with the absorption of the elements of water. From a purely chemical point of view it is not easy to imagine how this conversion of an aromatic into a fatty body can readily take place in the plant. A good deal may, however, be said in favour of the other view. If we accept Baeyer's above-mentioned suggestion, that formic aldehyde is the immediate product of assimilation, we may follow him in regarding it as giving rise by condensation to the polymeric substance glucose, or to starch, the anhydride of glucose. That a process of this kind is not impossible is shown by the fact that Butlerow succeeded in producing a saccharoïd substance from formic aldehyde by the action of alkalis. If this be the process which actually occurs in the plant the function of chlorophyll is simply

* *Biologie von Monotropa.* 1873.

† *Comptes rendus*, lxxvi, and *Ann. d. Sci. Nat.* 1874.

‡ *Experimental-Physiologie*, p. 315.

§ *Sitzungsber. d. Wien. Akad. Math.-naturw. Classe*, liv.

the decomposition of carbonic anhydride into carbonic oxide and oxygen.

At present there are no facts which could be brought forward to prove either the one or the other of these two hypotheses, and the question of the part played by chlorophyll in the process of assimilation must for the present remain an open one. It is interesting, however, to note in connection with this subject the importance of the salts of potassium (more particularly the chloride and nitrate), in the process. Speaking generally, it may be said that no appreciable increase in weight takes place in a plant—that is, that the plant does not assimilate—from which all supplies of potassium salts are cut off.* Liebig long ago pointed out that potassium salts always occur in considerable quantity in those parts of plants in which carbohydrates are being formed or deposited, and he explained the fact in a manner which will be subsequently discussed, and shown to be unsatisfactory. It may be that the alkali is liberated from its combination, and is then available for use in the formation of carbohydrates from the first products of assimilation in the manner above mentioned.

In concluding this portion of the subject, I will mention very briefly the probable fate of the carbohydrates—the raw material of the plant—formed by assimilation. One portion becomes converted into cellulose to form the walls of the cells in growing organs, and this cellulose becomes subsequently converted into lignin or cork, or gum or mucilage. A second portion is devoted to the nutrition of the existing protoplasm, and to a formation of new proteid material by the combination of carbohydrates with derivatives of the nitrogenous compounds (ammonia and nitrates) absorbed by the roots. We have at present no certain knowledge of the nature of this important process, the investigation of which offers a promising field for research. The researches which have been made in this direction all tend to prove its actual occurrence, but the results obtained are not sufficiently definite to afford a satisfactory explanation of it. Time will not permit me to do more than refer to the researches of Schutzenberger† upon albuminoïd substances. He finds that not only do such substances as chondrin and chitin ("*véritables glucosides azotés complexes*") exist, which, as is well known, yield on decomposition glucose and various nitrogenous substances, but that the true albumins contain, as an integral part of their molecule, amides of cellulose (*amides cellulosiques*). A third portion probably undergoes decomposition to form the colouring matters, acids, &c., and furnishes in consequence energy to the plant, and the remainder of the carbohydrates is stored up in the

* Nobbe, *Ueb. die organische Leistung des Kaliums in der Pflanze.* 1871.

† *Les fermentations.* 1876.

persisting parts of the plant, either as carbohydrate, or as oil and fat.

We may now pass on to consider the physiological significance of some other substances which are found in the cells of plants, in the same manner as we have done that of chlorophyll. Those which occur most frequently are the numerous colouring matters, the vegetable acids, the glucosides, and the alkaloïds. Of these I propose to select the acids, partly because their function is more fully understood and their chemical constitution is more clearly known than is the case with the other substances, but more especially because they have been connected by some great authorities with the subject which we have just discussed.

Mulder and Liebig * considered that the first products of assimilation were the vegetable acids, which combined with bases derived from the soil to form salts, and in this way Liebig explained how it is that a plant will not grow in a soil which does not contain a certain proportion of bases. This view was supported by Berthelot, who showed that carbonic oxide will combine directly with water to produce formic acid—

$$CO + H_2O = CH_2O_2.$$

On the other hand, Davy considered that the first products of assimilation were neutral substances, such as dextrin and sugar, a view which was also held by the botanists von Mohl,† Schleiden, Schacht, and others. They regarded the vegetable acids as being produced by the oxidation of the organic substances of the plant, a view which, as we shall see, has much in its favour.

The fact which afforded the strongest evidence in favour of Liebig's view was the gradual diminution in the acidity of ripening fruits, which he attributed to the conversion of the acids into sugar. This he regarded as a striking example of the process which, according to his views, takes place in every assimilating organ. It is very strange that no attempt was made to verify this hypothesis by estimating the amount of acids in a fruit at various stages of development. The mere disappearance of the strongly acid taste and the increasing sweetness afford no conclusive evidence that the acids have undergone conversion into sugar. The change of flavour may be as satisfactorily accounted for in a variety of ways; for instance, by supposing that the acids are gradually neutralised, and that sugar is brought to the ripening fruit from other parts of the plant. It is obvious that the experimental evidence cited in support of Liebig's view completely breaks

* *Agricultural Chemistry;* see also Rochleder, *Chemie und Physiologie der Pflanze*, 1858, for a discussion of the subject.

† *Anatomy and Physiology of the Vegetable Cell*, 1852, p. 90.

down, and the theory is totally demolished by the consideration that if acids are the first products of assimilation, it is impossible that the volume of oxygen exhaled should be equal to that of the carbonic anhydride absorbed, a proportion which we have already found to have been accurately determined.

We have now to consider the other view, according to which the vegetable acids are products of the oxidation of the organic substance of the plant. The supporters of this theory did not bring forward any definite experimental evidence in its favour, for they probably considered that the *onus probandi* lay rather upon those who controverted it. Von Mohl, however, pointed out the important fact that the vegetable acids occur in very many plants deposited in their cells as insoluble salts, for the most part of lime; and the researches of Hilgers* upon the formation of calcic oxalate in the parenchyma of Monocotyledons, show that the crystals when once fully formed undergo no further change. This fact affords a strong argument against Liebig's view of the derivation of plastic substance from acids, and suggests that substances which are thus for ever removed from the active metabolism of the plant, are to be regarded as by-products of some of the various processes which are included under that expression.

With which of these processes are we to associate the formation of the acids in the plant? At present it is impossible to give a satisfactory reply to this question, but it seems reasonable to suggest that they may be formed in connection with the process of respiration—a process which is essentially one of oxidation, though as yet there is no decisive evidence to show that this is actually the case. However, it has long been known that acids, more particularly formic and oxalic, may be produced by the oxidation of various vegetable substances, such as starch, sawdust, &c., and that if the process be carried far enough, carbonic anhydride and water are the final products. Hoppe-Seyler† found that, on treating grape sugar with alkalis, the access of oxygen being prevented as far as possible, it was decomposed into formic and carbonic acids and pyrocatechin, and further, that on heating starch with water in closed tubes, pyrocatechin, together with formic acid and carbonic anhydride (formed perhaps by the decomposition of oxalic acid), were produced. These facts suggest the inference that something of the same kind may occur in the living plant; that carbohydrates are split up into acids and aromatic substances; that a portion of the acid thus produced combines with the

* *Ueber das Auftreten der Krystalle von oxalsaurem Kalk im Parenchym einiger Monocotylen.* Jahrb. fur Wiss. Bot., Bd. vi, 1867.

† *Medicinish-Chemische Untersuchungen.* 1866–71, p. 586.

oxybenzenes, with elimination of water, to form chlorophylloïd colouring matters; and that the remainder is either neutralised and deposited as crystals of insoluble salts in the cells of the plants, or is decomposed into carbonic anhydride and water. Karl Kraus* has shown that one part, at any rate, of this hypothesis admits of experimental proof. He finds that the external dry scales of the onion contain crystals of calcic oxalate and pyrocatechin, but no grape-sugar; whereas the internal juicy scales contain much grape-sugar, but neither calcic oxalate nor pyrocatechin. If, however, the internal scales be allowed to become dry, they assume the brown colour of the external scales, the grape-sugar disappears from the cells, and pyrocatechin and crystals of calcic oxalate make their appearance.

It may, therefore, be regarded as a fact that acids are formed from carbohydrates in the living plant by a process of decomposition, which is necessarily one of oxidation. That this is the case is shown by the following equations:—In the first, 2 molecules of grape-sugar are regarded as giving rise to 1 molecule of pyrocatechin and to 1 of oxalic acid, with evolution of carbonic anhydride and formation of water, 5 molecules of oxygen being required:

$$2C_6H_{12}O_6 + 5O_2 = C_6H_6O_2 + C_2H_2O_4 + 4CO_2 + 8H_2O.$$

In the second, 2 molecules of grape-sugar are regarded as giving rise to 1 molecule of pyrocatechin and to 3 of oxalic acid, no carbonic anhydride, but only water being formed, and 4 molecules, the minimum quantity, of oxygen being required:

$$2C_6H_{12}O_6 + 4O_2 = C_6H_6O_2 + 3C_2H_2O_4 + 6H_2O.$$

With reference to the connection of this formation of acids with the respiration of the plant, it is to be noted that possibly it may be accompanied by an evolution of carbonic anhydride, as is shown in the first equation, even when so highly oxidised an acid as oxalic is the product, and that when a less highly oxidised acid is produced, the evolution of carbonic anhydride is inevitable. The following equation illustrates this with regard to an acid of frequent occurrence in plants, the tartaric—

$$2C_6H_{12}O_6 + 3O_2 = C_6H_6O_2 + C_4H_6O_6 + 2CO_2 + 6H_2O.$$

Whether it be or be not admitted that the formation of acids in the plant is accompanied by an evolution of carbonic anhydride, it is certain that this is one of the products of their final decomposition. It must be remembered that oxalic acid is singular among the acids occurring in plants in being deposited in an insoluble form, and in being thus excluded from any further participation in the active

* *Flora.* 1875, p. 253.

chemical processes. The other acids remain for the most part dissolved in the cell-sap of living cells under circumstances which favour their further oxidation.

The whole subject may be thus briefly summed up. The decomposition of carbohydrates gives rise in the first instance to substances (oxybenzenes) which contain a smaller proportion of oxygen in their molecule, and to substances (acids) which contain a larger proportion. Probably the acids first formed contain a relatively small proportion of oxygen, and are capable of further oxidation, each process of oxidation giving rise to a substance with an increased proportion of oxygen in its molecule, until carbonic anhydride is formed as the final product.

I will add only a few words as to the function discharged by the acids in the economy of the plant. All that is known on this subject has reference more particularly to oxalic acid. It appears from the researches of Holzner* and of Emmerling,† that the oxalic acid formed in the plant decomposes phosphates, sulphates, and nitrates, and sets the acids at liberty to be used in the nutrition of the tissues.

There is yet one more substance of particular interest to which I would draw your attention. This substance is asparagine. It has been found to occur in very many plants, and is particularly abundant in those which have undergone etiolation. Its physiological significance has, however, been made clear in the case of leguminous plants. Baeyer‡ has shown that in *Lupinus luteus*, as the legumin gradually diminishes in the cotyledons of the seedling, so does asparagine gradually increase in quantity in the stem and roots. From this it is inferred that the legumin stored up in the cotyledons is made available for the nutrition of the seedling by conversion into a soluble and diffusible substance. The researches of Pfeffer§ show that if the seedling be kept in the dark, the conversion of legumin into asparagine proceeds, but that the asparagine accumulates in the cells. He finds that this is the case also if the seedling be exposed to light in an atmosphere which contains no carbonic anhydride.

It appears therefore that the asparagine can only be made available if the process of assimilation be allowed to proceed. The probable explanation of this is that asparagine combines with the carbohydrates formed by assimilation to reproduce proteïd substance.

We have therefore a tolerably clear general idea of the origin and use of asparagine in these plants, but many details have yet to be sup-

* *Flora.* 1867.
† *Ber. d. Deut. Chem. Ges.* 1872.
‡ *Landwirthsch. Versuchs.-Stat.*, vol. ix.
§ *Jahrb. f. Wiss. Bot.*, viii. 1872.

plied. The actual mode of origin, for instance, of asparagine from the reserve proteïds has not yet been fully explained.

Since the total amount of nitrogen contained in the seed does not vary throughout the whole process of germination, whereas oxygen is absorbed and carbonic anhydride is evolved, the formation of asparagine is usually regarded as being the result of a simple process of oxidation. Von Gorup-Besanez* has, however, shown that a peptic ferment exists in the germinating seeds of leguminous plants (vetches), and it seems therefore pertinent to enquire whether or not this ferment has anything to do with the production of asparagine which they contain in such abundance. According to Hoppe-Seyler† leucine and tyrosine are produced when proteïds are submitted to long-continued gastric digestion, and it is admitted on all hands that they are formed when proteïds undergo pancreatic digestion. It is interesting to note here that von Gorup-Besanez‡ has detected leucine in the germinating seeds of leguminosæ. Further, Radziejewsky and Salkowsky§ have shown that aspartic acid is one of the products of the pancreatic digestion of fibrin, and Knieriem‖ has proved the same in the case of gluten. It is well known how readily asparagine can be decomposed into aspartic acid and ammonia, and it may therefore be fairly assumed that in these digestive experiments the occurrence of aspartic acid among the final products is an indication that asparagine has been formed during the process. These facts afford some ground for regarding the formation of asparagine in germinating seeds as dependent, not upon simple oxidation, but upon the action of the proteolytic ferment which they contain.¶ It is worthy of note that the reaction of germinating seeds is acid; if therefore asparagine be produced in them by the agency of a proteolytic ferment, a well-marked distinction is set up between it and the pancreatic ferment (trypsin), for the latter can form aspartic acid only in an alkaline fluid.

Further researches are required to elucidate these points, and perhaps they may succeed in enabling us to connect these products of decomposition with certain groups of proteïds, as, for example, asparagine with the caseins, and leucine with the albumins and globulins of the seed. That something of this kind is the case is suggested by the

* *Ber. d. Deut. Chem. Ges.*, vii. 1874.

† *Physiologische Chemie*, ii Theil. 1878, p. 228.

‡ *Ber. d. Deut. Chem. Ges.*, vii; see also Cossa, *ibid.*, viii.

§ *Ber. d. Deut. Chem. Ges.*, vii. 1874.

‖ *Zeitschr. f. Biologie*, Bd. ii.

¶ The detection of tyrosin (together with aspartic acid) in seedlings of *Cucurbita*, by E. Schultze and J. Barbieri (*Ber. d. Deut. Chem. Ges.*, xi, 1878), tends to confirm this view.

fact that the seed of the castor-oil plant, according to Ritthausen, contains no legumin, and Pfeffer was unable to discover any asparagine in the seedling.

It appears that other substances exist which are analogous to asparagine in their physiological significance. Such are solanine and chenopodine, for example. The former has been usually regarded as an alkaloïd, but it has not been suggested that it may be allied to asparagine in its chemical constitution.* The latter has been shown by Dragendorff† to be probably identical with leucine.

Although I have by no means exhausted the points of chemical interest which present themselves in the physiology of plants, I am compelled to content myself with those which I have brought to your notice. The account which I have given of them will suffice to show that the physiologist has already received much assistance from the chemist in his attempts to explain the phenomena of plant life, but it suggests at the same time that further assistance of the same kind is yet required. The researches above mentioned of Adolf Baeyer may be cited as a striking example of the valuable aid which the chemist can afford to the physiologist, and of the particular kind of information which the physiologist is anxious to obtain. The importance of various substances in the economy of the plant, and the conditions under which these substances are formed, can only be fully understood when we are in possession of accurate quantitative estimations of the amount of such substances present in the plant under different circumstances. These determinations involve considerable difficulties, for it is by no means easy to extract the whole amount of a substance present in a plant from the cells in which it occurs, and the isolation of the substance when extracted is even more perplexing. These difficulties, however, are doubtless to be overcome by patient endeavour, and by the gradual improvement of the chemical methods employed.

XLV.—*On some Fluorine-Compounds of Vanadium.*

By H. Baker, Student in the Chemical Laboratories of The Owens College, Manchester.

Although no fluorides or oxyfluorides of vanadium have been described, it would appear from the general relationships of the metal that a series of vanadium oxyfluorides corresponding with those of niobium discovered by Marignac (*Compt. rend.*, lx, 234, 1355; *Ann. Chem.*

* For the literature on this subject, see *De Vries-Landwirthsch. Jahrb.* 1878.

† See Husemann, *Pflanzenstoffe.*

Pharm., cxxxv, 49; cxxxvi, 295; *Archives des. Sc. Phys. et Nat.*, xxiii, 278) might probably be obtained.

The following investigation was undertaken to determine the mode of formation and properties of the fluoxyvanadates:—

A. Potassium Fluoxyvanadates.

I. *Lamellar Potassium Fluoxyvanadate*, $6KF.V_2O_5.2VOF_3 + 2H_2O$.

Vanadium pentoxide dissolves in an aqueous solution of hydrogen potassium fluoride readily, and with a considerable rise of temperature. The solution on cooling deposits yellowish crystalline globules composed of an aggregation of small plates—probably hexagonal—having a pearly lustre, which cannot be obtained in a more definitely crystalline form. The salt dissolves in water, yielding a deep yellow solution, having an acid reaction. The dry salt does not smell of hydrofluoric acid, and when it is laid on glass the latter is but slowly attacked; it is insoluble in and unacted on by cold concentrated sulphuric acid.

The fluorine in almost all these compounds was determined by dissolving a weighed quantity of the salt in water, adding ammonium carbonate to alkaline reaction, precipitating with calcium chloride solution, and evaporating the whole to dryness. The solid residue was then treated with acetic acid, the excess of acid driven off, water added to the residue, and the precipitate filtered and washed. This precipitate, containing calcium fluoride and vanadium pentoxide, was then dried and heated with strong sulphuric acid, the liquid diluted with a small quantity of water, alcohol added, and after standing, the calcium sulphate was collected and weighed, the weight of the fluorine being calculated from this.

The potassium was determined in another portion of the salt by precipitating the solution with lead acetate, filtering, and removing the excess of lead by sulphuretted hydrogen. The filtrate, after addition of sulphuric acid, was evaporated to dryness, ignited, and the potassium sulphate weighed.

The water was always determined from the loss of weight on ignition in contact with a large excess of lead oxide.

Another portion was heated with strong sulphuric acid, the solution diluted and reduced with sulphurous acid. After boiling off the excess of the latter, the vanadium was determined by a standard solution of potassium permanganate. The following are the analytical results:—

1st Preparation.—0·2267 required 13·72 c.c. $KMnO_4$ solution (1 c.c. = 0·007935 V_2O_5); 0·4398 gave 0·2934 K_2SO_4; 0·4085 gave 0·2618 K_2SO_4; 0·3173 gave 0·2002 CaF_2; 0·2770 gave 0·1125 CaO (= CaF_2); 0·2080 lost 0·0085 H_2O; and 0·2625 lost 0·0125 H_2O.

2nd Preparation.—0·3745 required 22·9 c.c. $KMnO_4$ solution (1 c.c. = 0·007953 V_2O_5); 0·4270 gave 0·2752 K_2SO_4; 0·4073 gave 0·3980 $CaSO_4$; 0·5595 gave 0·5566 $CaSO_4$; and 0·3559 gave 0·0181 H_2O.

3rd Preparation.—In this case the potassium hydrogen fluoride and vanadium pentoxide were used in the ratio given by the above analyses, viz., $3KHF_2 + V_2O_5$. 0·5095 required 25·9 c.c. $KMnO_4$ solution, and gave 0·3410 K_2SO_4: 0·4345 required 22·2 c.c. $KMnO_4$ solution, and gave 0·2940 K_2SO_4; 0·4330 gave 0·4060 $CaSO_4$; and 0·4687 gave 0·4775 $CaSO_4$. Hence we have:—

	Found.							Calculated for $6KF.V_2O_5.2VOF_3.2H_2O$.
	1.		2.		3.		Mean.	
V ..	26·99	—	27·35	—	27·11	27·25	27·18	25·18
K ..	29·99	28·75	28·94	—	30·05	30·38	29·64	28·78
F ..	30·70	27·50	27·24	27·73	26·13	28·40	27·95	27·89
H_2O	4·09	4·76	5·10	—	—	—	4·65	4·41
O ..	—	—	—	—	—	—	—	13·73
	—	—	—	—	—	—	—	99·99

II. *Acicular Potassium Fluoxyvanadate*, $3KHF_2.2VOF_3$.

On dissolving the preceding salt in warm aqueous hydrofluoric acid (an excess of acid does not decompose the salt), an almost colourless salt separates out on cooling, in the form of long thin needles grouped in tufts and brushes. The dry salt smells of hydrofluoric acid, acts rapidly on glass, and is at once decomposed by cold concentrated sulphuric acid with effervescence.

Preparation 1.—0·3130 required 14·55 c.c. of $KMnO_4$ solution, and 0·4895 gave 0·2642 K_2SO_4.

Preparation 2.—0·1895 required 9·3 c.c. $KMnO_4$ solution; and 0·5888 required 29·6 c.c. $KMnO_4$ solution, and gave 0·3350 K_2SO_4; 0·4194 gave 0·6905 $CaSO_4$; 0·3770 lost 0·0212 H_2O.

Preparation 3.—0·3772 required 14·15 c.c. $KMnO_4$ solution; 0·5318 required 21·05 c.c. $KMnO_4$ solution, and gave 0·2855 K_2SO_4; 0·3550 gave 0·5852 $CaSO_4$; 0·4870 gave 0·8055 $CaSO_4$; 0·4680 gave 0·0250 H_2O. Hence—

	Found.						Calculated for $3KHF_2.2VOF_3$.
	1.	2.		3.		Mean.	
V..	20·74	21·14	22·48	20·00	21·09	21·09	21·28
K..	25·17	—	25·54	—	24·11	24·98	24·32
F..	—	45·90	—	45·94	46·10	45·98	47·14
O..	—	—	—	—	—	—	6·63
H..	—	—	—	—	—	—	0·62
	—	—	—	—	—	—	99·99
H_2O	—	5·63	—	5·34	—	5·48	5·59

No compound richer in potassium than the preceding is obtained by addition of potassium hydrogen fluoride to this salt, even when five or six parts of potassium hydrogen fluoride are present to one part of the vanadium salt, the latter crystallising out unaltered, as is seen in the following analyses:—

1*st Preparation.*—0·2710 required 10·9 c.c. $KMnO_4$ solution.

2*nd Preparation.*—0·6230 required 24·8 c.c. $KMnO_4$ solution.

	Found.		Calculated for $3KHF_2.2VOF_3$.
	1.	2.	
V p. c.	21·44	21·22	21·28

B. Ammonium Fluoxyvanadates.

Vanadium pentoxide readily dissolves in a solution of ammonium hydrogen fluoride, and to a very considerable extent. The solution, which is very rich in vanadium, does not crystallise on standing, but when more of the ammonium-hydrogen fluoride is added small slightly yellow pearly plates of the lamellar ammonium fluoxyvanadate separate out, the liquid often solidifying, owing to the quantity thrown down. If these pearly crystals be dissolved, and if more ammonium-hydrogen fluoride be added, the solution deposits a bright yellow crystalline precipitate of the pyramidal ammonium fluoxyvanadate. Further addition of ammonium-hydrogen fluoride produces no change.

A third ammonium fluoxyvanadate is obtained by dissolving the pyramidal salt in warm aqueous hydrofluoric acid. On cooling, the acicular ammonium fluoxyvanadate separates in pale yellowish needles or fine prisms.

I. *Lamellar Ammonium Fluoxyvanadate*, $6NH_4F.V_2O_5 2VOF_3 + 2H_2O$.

This forms small transparent hexagonal plates, extremely thin, of a pale yellowish colour, and having a beautiful pearly lustre. The angles were measured with a microscope goniometer, the deviations from a hexagonal plate being within observational error, viz., 120° 34′ instead of 120°, and 60° 36′ instead of 60°. It is readily soluble in water, and is unacted on by cold concentrated sulphuric acid.

The vanadium in these salts was generally estimated by igniting with sulphuric acid and weighing the residual vanadium pentoxide. The ammonia was estimated by distilling it into a known excess of normal hydrochloric acid, and titrating with normal soda solution.

1*st Preparation.*—0·2600 gave 0·3144 $CaSO_4$; 0·2315 gave NH_3 sufficient to neutralise 2·1 c.c. normal HCl.

2*nd Preparation.*—0·6968 required 6·5 c.c. normal HCl; 0·3646 gave 0·1980 V_2O_5; 0·3044 gave 0·1670 V_2O_5; 0·4815 gave 0·5620 $CaSO_4$; 0·4110 lost 0·1394 on ignition with lead oxide = $NH_3 + H_2O$; and 0·3785 lost 0·1076.

	Found.				Calculated for $6NH_4F.V_2O_5.2VOF_3.2H_2O$.
	1.	2.		Mean.	
V.....	—	30·53	30·83	30·68	29·81
F.....	33·75	32·53	—	33·14	33·02
NH_4....	16·37	16·83	—	16·00	15·71
O.....	—	—	—	—	16·25
H_2O....	—	—	—	—	5·22
	—	—	—	—	100·00
Loss....	—	28·39	28·43	28·41	27·90

II. *Pyramidal Ammonium Fluoxyvanadate*, $12NH_4F.V_2O_5.2VOF_3$.

Has a fine yellow colour, closely resembling potassium chromate. Its aqueous solution is yellow, and has an acid reaction. It is unacted on by cold concentrated sulphuric acid.

The exact measurement of the crystals was rendered difficult, inasmuch as their faces were invariably rough. It was, however, readily seen that their form is that of a simple pyramid, without any modifications whatever. The angles are nearly those of an octohedron, but their action on polarised light shows that the crystals are not regular.

Preparation 1.—0·4035 required 5·63 normal HCl, and 18·05 c.c. $KMnO_4$ solution: 0·3910 required 5·43 normal HCl; 0·1635 required 7·35 c.c. $KMnO_4$ solution; 0·3542 gave 0·4903 CaSO4.

Preparation 2.—0·2878 required 12·8 c.c. $KMnO_4$ solution; 0·6555 required 9·1 c.c. normal HCl; 0·4330 gave 0·6255 $CaSO_4$; and 0·3170 ignited with PbO lost 0·1140.

	Found.				Calculated for $12NH_4F.V_2O_5.2VOF_3$.
	1.		2.	Mean.	
V.....	23·85	23·97	23·71	23·84	23·48
NH_4....	25·18	25·05	24·99	25·07	24·73
F.....	38·59	—	40·25	39·42	38·98
O.....	—	—	—	—	12·79
	—	—	—	—	99·99
Loss....	—	—	35·96	35·96	35·71

III. *Acicular Ammonium Fluoxyvanadate*, $3NH_4HF_2.2VOF_3$.

This salt when dry smells of hydrofluoric acid, and turns rapidly red when laid on glass, owing to separation of vanadium pentoxide. It effervesces with cold sulphuric acid. The aqueous solutions of this salt, as well as of the lamellar ammonium salt, have a great tendency on crystallising to run up the sides of the vessel. Although the analyses do not give very exact results, they still exhibit an amount of agreement which, coupled with the appearance and properties of the salt, show it to be different from the other two ammonium compounds. It is probably analogous to and isomorphous with the potassium salt $3KHF_2.2VOF_3$.

	Found.						Calculated for $3NH_4HF.2VOF_3$.
	1.	2.		3.	4.		
V.....	26·51	23·85	—	26·02	22·20	21·93	24·49
NH_4....	15·15	16·44	16·54	15·24	13·60	—	12·91
F.....	—	59·27	—	53·04	54·55	—	54·26
Loss....	—	27·55	—	—	—	—	25·07

This acicular salt is decomposed by an excess of hydrofluoric acid. A sample was prepared and recrystallised from hydrofluoric acid (of 22 per cent.), when it contained 19·31 per cent. vanadium; again recrystallised from hydrofluoric acid, it contained 12·48 per cent. vanadium; and by again recrystallising from acid the vanadium was reduced to 3·70 per cent.

A solution of vanadium pentoxide, ammonium fluoride, and hydrofluoric acid, in the proportions in which they are present in the

pyramidal salt, deposited none of the latter, but a very small quantity of the lamellar salt, much more of which was thrown down by further addition of ammonium fluoride, so that in preparing these salts a decided excess of ammonium fluoride must be used, especially in the case of the pyramidal salt, although too large an excess must be avoided, as it also crystallises out.

C. Zinc Fluoxyvanadate, $ZnF_2.ZnO.2VOF_3 + 14H_2O$.

To obtain the vanadium compound corresponding with Marignac's zinc fluoxyniobate, $NbOF_3.ZnF_2 + 6H_2O$, zinc carbonate and vanadium pentoxide were dissolved in the requisite proportions in hydrofluoric acid. The solution when allowed to evaporate deposited hard yellow crystals, whilst the syrupy mother-liquor generally contained some fine acicular crystals. By pouring off the mother-liquor and washing with small quantities of water, the acicular crystals are dissolved, whilst the hard yellow ones remain unattacked. Zinc fluoxyvanadate forms hard yellow monoclinic prisms, having the forms $\infty P . \infty \breve{P}\infty . \infty \bar{P}\infty . OP . + \bar{P}\infty$ with the approximative values $a : b : c = 0{\cdot}93 : 1 : 0{\cdot}83$, $L = 46°$, Fig. 1. The zinc was determined by heating with sulphuric

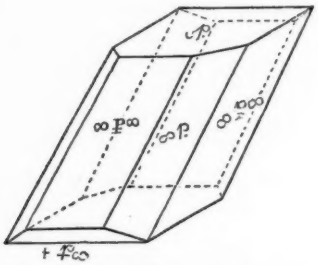


Fig. 1.—Zinc Fluoxyvanadate.

acid to drive off hydrofluoric acid, diluting, precipitating with sodium carbonate, and weighing the precipitate consisting of ZnO and V_2O_5. The vanadium was then estimated by means of potassium permanganate solution, and the quantity of zinc oxide obtained by difference.

1*st Preparation.*—0·3080 required 8·9 c.c. $KMnO_4$ solution; 0·4635 gave 0·1152 ZnO; 0·4835 gave 0·1174 ZnO, and required 14·1 c.c. $KMnO_4$ solution for the total vanadium; 0·5305 gave 0·4035 $CaSO_4$; 0·5675 gave 0·4570 $CaSO_4$; 0·6055 lost 0·2290 H_2O; and 0·5335 lost 0·2005 H_2O on ignition with lead oxide.

2*nd Preparation.*—0·1880 required 5·6 c.c. $KMnO_4$ solution; 0·3090 gave 0·0765 ZnO, and required 9·1 c.c. $KMnO_4$ solution; 0·2704 gave 0·2093 $CaSO_4$; 0·2855 lost 0·1088 H_2O.

	Found.					Calculated for $ZnF_2.ZnO.2VOF_3.14H_2O$.
	1.		2.		Mean.	
V.....	15·25	15·40	15·88	15·55	15·51	15·00
Zn.....	19·95	19·50	19·87	—	19·77	19·03
F.....	21·19	22·44	21·58	—	21·73	22·16
H_2O....	37·81	37·58	38·12	—	37·83	36·80
O.....	—	—	—	—	—	7·01
	—	—	—	—	—	100·00

This salt is slowly decomposed on exposure to the air, becoming covered with a brown or bright red coating.

D. Ammonium Fluoxyhypovanadate, $2NH_4F.VOF_2 + H_2O$.

A hydrofluoric acid solution of hypovanadic oxide (V_2O_4) was prepared by passing sulphuretted hydrogen into a hydrofluoric solution of the pentoxide, concentrating, and filtering. If ammonium fluoride be added to this solution, clear blue monoclinic crystals separate out, having the forms ∞P . OP, sometimes with a trace of $+P$. ∞P : ∞P (in orthodiagonal section) = 65° 6′; OP : ∞P (right) = 48° 28′; (left) = 48° 20′. Hence the form is monoclinic with OP : ∞P (mean) = 48° 24′. Then $a : b = 0{\cdot}9653 : 1$, and L = 38° 2′ (Fig. 2). Its aqueous solution is precipitated by alcohol. It is not attacked by cold sulphuric acid.

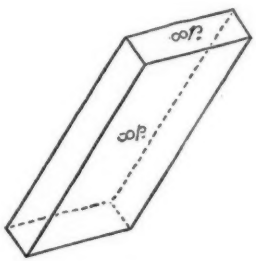


Fig. 2.—Ammonium Fluoxyhypovanadate.

Preparation 1.—0·2460 gave 0·1135 V_2O_5; 0·8180 required 8·3 c.c. normal HCl; 0·5990 gave 0·8610 $CaSO_4$; 0·4490 lost 0·1590 on ignition with lead oxide = $NH_3 + H_2O$; and 0·5885 lost 0·2160.

Preparation 2.—0·2665 gave 0·1245 V_2O_5; 0·5835 gave 0·9015 $CaSO_4$.

	Found.			Calculated for $2NH_4F.VOF_2.H_2O$.
	1.	2.	Mean.	
V.....	25·93	26·25	26·09	26·03
NH_4....	18·31	—	18·31	18·29
F.....	40·05	43·04	41·54	38·44
H_2O....	—	—	—	9·12
O.....	—	—	—	8·11
	—	—	—	99·99
Loss....	35·42	—	35·42	35·52

Although the above described salts resemble in character Marignac's fluoxyniobates; yet none of them are exactly analogous to any prepared by him. This is seen from the following list:—

Fluoxyvanadates.	*Fluoxyniobates.*
$6KF.V_2O_5.2VOF_3.2H_2O$, hexagonal laminæ.	$2KF.NbOF_3.H_2O$, monoclinic laminæ.
$6NH_4F.V_2O_5.2VOF_3.2H_2O$, hexagonal laminæ.	$2NH_4F.NbOF_3.H_2O$, monoclinic laminæ.
$3KHF_2.2VOF_3$, acicular needles.	$3KF.NbOF_3$, cuboïd forms.
$3NH_4HF_2.2VOF_3$, acicular needles.	$3NH_4F.NbOF_3$, cuboïd forms.
$12NH_4F.V_2O_5.2VOF_3$, pyramidal form.	$5KF.3NbOF_3.H_2O$, hexagonal prisms.
$ZnF_2.ZnO.2VOF_3(H_2O)_{14}$, monoclinic.	$5NH_4F.3NbOF_3.H_2O$, hexagonal prisms.
	$3KF.HF.NbOF_3$, monoclinic needles.
	$4KF.3NbOF_3.2H_2O$, triclinic prisms.
	$2KF.NbF_5$, acicular monoclinic crystals.
	$NH_4F.NbOF_3$, rectangular prisms.
	$3NH_4F.NbOF_3.NbF_5$, short prisms.
	$Zn.F_2.NbOF_3.6H_2O$, hexagonal.

Ammonium fluoxyhypovanadate.

$2NH_4F.VOF_2.H_2O$, monoclinic.

XLVI.—*On Ammonium Triiodide.*

By George Stillingfleet Johnson, Daniell Scholar of King's College, London.

Until quite recently I have refrained from attempting to prepare a periodide of ammonium, partly on account of the reported instability of its protiodide, but chiefly because it was believed that one result of the action of excess of iodine upon ammonium iodide would be the formation of iodide of nitrogen in large quantity. During some experiments, however, undertaken to establish the rational formula of the complicated polyiodide of lead, described in the Chemical Society's Journal for May, 1878 (p. 189), I passed ammonia gas into the mother-liquor of that salt to saturation. A yellow precipitate was produced, which was not explosive; but, on analysis, proved to be simply oxyiodide of lead ($PbI_2.PbO.H_2O$). The ammoniacal liquid still remained dark brown, but deposited no iodide of nitrogen.

Ammonia gas was now passed into the mother-liquor of potassium triiodide, as long as it was absorbed. The black liquid, whether aqueous or alcoholic, absorbed a large volume of the gas, with extrication of much heat, but without any change of colour or the formation of any precipitate. A number of cubical dark-coloured crystals separated out on cooling, which were roughly analysed, and appeared to have some such composition as $NH_4I_3.7KI$. The dark-coloured ammoniacal liquid filtered from these crystals, when allowed to evaporate gradually over strong sulphuric acid, deposited crystals of an apparently definite body, having the formula, $5NH_4I_3.KI$. There was no formation of iodide of nitrogen.

Encouraged by these results to proceed with the investigation, I now dissolved iodine to saturation in a strong aqueous solution of ammonium iodide. The iodine was dissolved very freely, with great lowering of temperature, and a black liquid was formed, without the production of any precipitate. In fact, the aqueous solution of ammonium iodide, when treated with excess of iodine, behaved in exactly the same way as a similar solution of potassic iodide.

With a view to the rapid production of crystals of ammonium triiodide, crystals of ammonium iodide and iodine were stirred with a small quantity of water, till the black liquid which resulted refused to dissolve more of either ingredient of the mixture. The saturated solution thus obtained was abandoned to evaporation over sulphuric acid. In a few days, it was obvious that crystallisation had commenced, for a dark-coloured crust had formed on the surface of the

University of Michigan

liquid. On removing this and pouring off the mother-liquor, the new salt was seen in the form of large, isolated crystals, having a great general resemblance to those of potassium triiodide.

The first analysis was made by applying a gentle heat to a weighed portion of the salt, so as to expel, if possible, the iodine in excess over NH_4I, and to observe the weight of the latter. Since the crystals do not fuse when heated, it was found necessary to add alcohol, to facilitate the removal of the iodine from the porous ammonic iodide in the crucible. It was also found to be impossible to avoid some loss of protiodide of ammonium by volatilisation during the process. The result was as follows:—

0·9275 gram of the dry crystals lost 0·6055 gram, or 65·28 per cent. NH_4I_3 contains 63·659 per cent. iodine in excess over NH_4I.

To determine more accurately the iodine in excess over NH_4I, known weights of the dry salts were dissolved in aqueous solution of potassic iodide, and the solution titrated with standard hyposulphite of soda, starch being employed as indicator.

Two samples of the crystals were analysed, and gave the following concordant results:—

Sample II.—(*a.*) 0·7685 gram of dry salt required 37·45 c.c. of hyposulphite solution, of which 1 c.c. = 0·0132 gram iodine. This is equivalent to 0·49434 gram of iodine, or 63·32 per cent. (*b.*) 0·3945 gram NH_4I_3 required 19·1 c.c. of the same hyposulphite solution, equivalent to 0·25212 gram iodine, or 63·908 per cent.

Sample III.—(*a.*) 0·358 gram of dry crystals required 17·65 c.c. of hyposulphite solution, of which 1 c.c. = 0·01283 gram iodine. This is equivalent to 0·2264495 gram iodine, or 63·25 per cent. (*b.*) 0·3965 gram of the salt required 19·6 c.c. of hyposulphite solution, equivalent to 0·251468 gram iodine, or 63·42 per cent.

The mean of these four determinations gives 63·474 per cent. The theoretical quantity required by the formula NH_4I_3, is 63·659 per cent. The *total* iodine was estimated as AgI by treating known weights of the dried compound with excess of solution of sulphurous acid gas in water, precipitating with excess of nitrate of silver, and acidulating the liquid with nitric acid. The argentic iodide was washed once or twice by decantation with hot water, acidulated with nitric acid, then transferred to a weighed filter, washed with boiling water, dried, and weighed. The results are as follow:—

(*a.*) *Sample* III.—2·4315 grams gave 4·301 grams of argentic iodide, equivalent to 2·3243 grams of iodine, or 95·55 per cent.

(*b.*) *Sample* IV.—0·883 gram gave 1·5575 grams AgI = 0·8417 gram of iodine, or 95·32 per cent.

The mean of these numbers gives 95·435 per cent. of iodine, whilst the compound NH_4I_3 would theoretically contain 95·488 per cent.

The *ammonia* present in the salt was determined by Nesslerizing a weak standard solution of ammonium triiodide in distilled water free from ammonia, and comparing the tint produced by it with that caused by a solution of ammonium chloride of known strength.

The standard solution of ammonium triiodide contained 0·0002082 gram NH_4I_3 in 1 c.c., whilst the ammonic chloride solution contained ·0000112 gram NH_3 in 1 c.c.

The results are as follow:—

(*a.*) 10 c.c. produced the same tint as 8 c.c. of NH_4Cl solution (1 c.c. of which = 0·0000112 gram NH_3), equivalent to 0·0000896 gram of NH_3, or 4·33 per cent.

(*b.*) 12 c.c. NH_4I_3 solution was equalised by 9·1 c.c. NH_4Cl solution. Hence NH_3 present = 0·00010192 gram, or 4·08 per cent.

(*c.*) 8 c.c. equalised by 6·4 c.c. NH_4Cl solution, equivalent to 0·00007168 gram NH_3, or 4·303 per cent.

The mean of these three ammonia determinations gives 4·237 per cent. NH_3, whilst the theoretical amount in NH_4I_3 is 4·26 per cent.

The triiodide of ammonium is a much more stable compound than the corresponding potassium salt. It crystallises in large tabular masses, the crystals being often isolated, and having almost exactly the same colour and lustre as the freshly prepared potassium triiodide. There appears to be very little tendency to the formation of long prisms, as is the case with the potassium salt.

As regards the action of solvents, the resemblance between the two compounds seems to be complete. A small quantity of water dissolves the crystals entirely, whilst an excess causes a precipitation of a large quantity of iodine (not iodide of nitrogen), the remainder being retained in solution by the ammonic iodide. As regards *deliquescence*, however, there is a marked difference between the triiodides of ammonium and potassium. The potassium salt becomes moist even in the comparatively dry air of a frosty day, whilst the ammonium compound deliquesces very slowly, even in a moist atmosphere. Indeed, I have kept some crystals of ammonium triiodide, which had been carefully dried between blotting paper, in a dry glass beaker simply covered loosely with a dial glass, for more than 12 hours, without any stain being observed on the glass; this, however, occurred during dry weather. On another occasion, some crystals of ammonium triiodide were exposed to air during wet weather: they liquefied entirely in about 24 hours. For two or three days subsequently the air was unusually dry, and at the end of that time the brown liquid had become a solid mass of crystals, though it had been subjected to no more powerful desiccating agent than tolerably dry air.

Again, the action of *heat* upon the two salts is also very different. Potassium triiodide fuses at about 45° C. without decomposition, but

ammonium triiodide does not melt when heated,; the form of the crystals is retained, but they become coated with white ammonium iodide, whilst vapours of iodine escape freely. Even at the ordinary temperature the crystals possess the odour of iodine. By a stronger heat the salt is volatilised completely, leaving no residue.

The salt is best preserved over quick-lime.

The *mother-liquor* of ammonium triiodide resembles that of the potassium compound in appearance and physical properties. Its specific gravity is 3·125, that of the mother-liquor of potassium triiodide being 3·13.

The *specific gravity* of the crystals of ammonium triiodide was determined by weighing them in their mother-liquor, since no other liquid appears to be without action upon them. The following results were obtained:—

I.	3·748	
II.	3·750	
	2)7·498	Mean 3·749.
	3·749	

It is remarkable that the specific gravity of the *crystals* of this salt should be higher than that of potassium triiodide, whose specific gravity is only 3·494. This may possibly be due to stronger chemical affinity between the atoms of the ammonium compound.

The *atomic volume* was determined by introducing weighed crystals of dry ammonium triiodide into a volumenometer flask, the neck of which was graduated in decigrams of water, the flask having been previously filled up to the zero-point with the mother-liquor of the salt.

The results are as follow:—

(I.) 1·2885 grams dry NH_4I_3 made the liquid rise 3·3 divisions. Atomic volume = 102·1.

(II.) 1·112 grams displaced 2·9 divisions. Atomic volume = 104·05.

The mean of these observations gives 103·07 as the atomic volume of NH_4I_3. The theoretical atomic volume is 106·4.

As the principal point of interest with regard to triiodide of ammonium appears to lie in a comparison between its properties and those of its potassium analogue, I have tabulated the principal points of difference between the two salts; thus:—

KI_3.	NH_4I_3.
Dark blue prisms. Usually elongated and aggregated.	Dark blue prisms. Usually tabular and isolated.
Extremely deliquescent.	Deliquescent only in moist air.
Fuses at 45° C., without decomposition.	Does not fuse when heated, but loses iodine, becoming coated with NH_4I.
Specific gravity of mother-liquor 3·13.	Specific gravity of mother-liquor 3·125.
Specific gravity of crystals 3·494.	Specific gravity of crystals 3·749.
Atomic volume 120·2.	Atomic volume 103·07.

Having definitely settled the existence and identity of ammonium triiodide, I hope now to investigate carefully the *double salts* which this compound may form with other iodides and periodides.

XLVII.—*On the Preparation of Salts of Nitrous Oxide.*

By A. E. Menke, Student in the Laboratory of King's College, London.

In the course of some analyses of cast-iron, an experiment was made to ascertain whether fusion with nitre and carbonate of soda would readily yield the phosphorus in the form of an alkaline phosphate.

If the operation be properly carried out, a bulky, yellow precipitate is obtained with nitrate of silver, which it is impossible to regard as phosphate. Professor Bloxam suggested the possibility of this body being the salt which Dr. Divers obtained by the action of sodium-amalgam on *nitrate of soda* (*Proc. Roy. Soc.*, xix, 425) and subsequent precipitation with silver nitrate. Several analyses of the silver salt were made.

Analysis of the Silver Salt.

The silver was estimated by dissolving in nitric acid and precipitating as chloride. Amount of substance taken = ·6625 gram. On boiling with a little nitric acid, a little silver chloride, existing as impurity, remained undissolved: this was collected on a filter, fused, and weighed, that adhering to the filter-paper being burnt to metallic silver. The amount of silver chloride found, including the metallic silver calculated as chloride, = ·092 gram, which when subtracted

from the amount of original substance taken, leaves ·5705 of the pure silver salt.

The solution in nitric acid was then precipitated with hydrochloric acid. The silver chloride was collected on a filter, fused and weighed. The amount of silver chloride found was ·599 gram. ·599 AgCl = 78·17 per cent. of silver.

A second analysis was made in a similar manner, the amount of substance taken being ·175 gram. The silver chloride found as impurity was ·014 gram, leaving ·161 gram of the pure silver salt.

The amount of silver chloride obtained from the nitric acid solution was ·167 gram. ·167 of silver chloride = 78·01 per cent. of silver.

	Pure substance taken.	Silver chloride found.	Per cent. of silver.
I.....	·5705	·5990	78·17
II.....	·1610	·1670	78·01

Mean = 78·09 per cent.

The amount of silver found, agrees, therefore, with the formula AgNO, which requires 78·26 per cent. of silver, and also with the analyses of Dr. Divers.

Sodium nitrate may be substituted for the potassium salt, and furthermore the admixture of carbonate of soda at first used may be left out, the salt being satisfactorily prepared by the simple fusion of iron filings with sodium nitrate. Regarding the best temperature for the operation, experiments were made with a Bunsen burner, a Gore's gas furnace, a coal furnace, and a charcoal furnace, the best results being obtained with a charcoal furnace. The silver precipitate is very bulky, but shrinks greatly when dried. The silver salt being reduced slightly at 100°, it is best to dry it in a vacuum over oil of vitriol, taking care to protect it from the light.

The silver salt is soluble in ammonia and in nitric acid, from solutions in either of which it can be again thrown down, as was shown by Dr. Divers, on the addition of acid in the one case, and of alkali in the other. When the silver salt is strongly heated it turns black owing to the reduction of the silver.

Preparation of the Sodium Salt.

To prepare the sodium salt, iron filings were fused with sodium nitrate in an iron crucible over a charcoal furnace, boiled with water, filtered from the oxide of iron, evaporated down to a small bulk, and left to crystallise. White needle-shaped crystals were deposited having the composition $NaNO + 3H_3O$.

In order to obtain the best yield of the salt the crucible ought to be kept at a red-heat for about an hour after the deflagration has taken

place, otherwise the sodium nitrate will not be properly converted into hyponitrite, and crystals will be got with great difficulty.

Analysis of the Sodium Salt.

The sodium was estimated by conversion into sulphate.

	Weight of substance taken.	Sodic sulphate found.	Per cent. of sodium.
I.....	·478	·313	21·19
II.....	·3995	·2615	21·20
III.....	·3309	·2215	21·39
IV.....	·2205	·1455	21·35

Mean = 21·28.

The water of crystallisation was next determined by drying at 100° C. in the water-bath until a constant weight was obtained, which generally took about three or four hours. The following are some of the results :—

	Weight of substance taken.	Loss.	Per cent. of water.
I.....	·202	·1025	50·74
II.....	·122	·0615	50·39
III.....	·442	·240	50·43
IV.....	·662	·350	50·62

Mean = 50·54.

The nitrogen was estimated by burning with soda-lime and passing the ammonia gas through standard sulphuric acid, also by precipitating as ammonio-platinic chloride. The following numbers are the results :

	Amount of substance taken.	Ammonia obtained.	Nitrogen per cent.
I.....	·466	·077129	12·95
II.....	·524	·0872175	13·70

	Amount of substance taken.	Ammonio-platinic chloride.	Nitrogen per cent.
III.....	·3625	·740	12·80

Mean = 13·15.

It will be seen that the mean numbers of the several analyses agree well with the formula $NaNO.3H_2O$:—

	Found.	Calculated.
Na =	21·26 per cent.	21·49 per cent.
N =	13·15 „	13·08 „
H_2O =	50·54 „	50·46 „
O =		14·95 „
		100·00

Experiments were then made, substituting zinc for iron in the reduction of the nitre, but the reaction was too violent, and there was not the slightest indication of the salt being formed.

The sodium salt is very soluble in water, to which it imparts a slightly alkaline reaction, but it is quite insoluble in ether and alcohol. It is also slightly efflorescent, and was found to lose water over sulphuric acid. I have not yet succeeded in obtaining crystals of the potassium salt.

An aqueous solution of the sodium salt was found to give the following reactions with some of the metals:—

With *copper sulphate*, a turquoise-blue precipitate soluble in acetic acid.

With *manganese sulphate*, a white precipitate soluble in acetic acid.

With *magnesium sulphate*, a white precipitate soluble in acetic acid.

With *bismuth nitrate*, a white precipitate insoluble in acetic acid.

With *zinc sulphate*, a white precipitate soluble in acetic acid.

With *aluminium sulphate*, a white precipitate insoluble in acetic acid.

With *baryta*, a white precipitate soluble in acetic acid.

With *calcium chloride*, a white precipitate soluble in acetic acid.

With *mercuric chloride*, a white precipitate, which afterwards became yellow and then brownish-red, which dissolved in acetic acid, leaving a white precipitate.

With *cobalt nitrate*, a mauve precipitate soluble in acetic acid.

With *mercurous nitrate*, a black precipitate, apparently metallic mercury at the bottom, and whitish-yellow suspended matter at the top, insoluble in acetic acid.

With *gold chloride* the gold was reduced to the metallic state as a purple powder.

With *platinic chloride*, a reddish-white precipitate, which on the addition of acetic acid was largely increased.

With *lead acetate*, a white precipitate, which was insoluble in acetic acid.

With *stannous chloride*, a white precipitate insoluble in acetic acid.

With *nickel sulphate*, a whitish-green precipitate soluble in acetic acid.

With *strontium nitrate*, a white precipitate soluble in acetic acid.

With a *cerous salt*, a white precipitate insoluble in acetic acid.

With *ferrous sulphate*, an olive-green precipitate resembling that obtained by caustic alkalis, and changing, on addition of acetic acid, to a yellowish precipitate.

With *ferric chloride*, a yellow precipitate soluble in acetic acid.

At the suggestion of Mr. Hartley, I acted upon the silver salt in a sealed tube with iodide of ethyl. As soon as the tube is sealed up,

ebullition commences. If heated in a water-bath for some hours the silver is converted into iodide. On fractionating the distillate, evidence of the formation of an ethereal salt of low boiling point is obtained. As the vapour-density of this would fix the molecular formula of the salt, I hope soon to be able to communicate success with further experiments in this direction.

XLVIII.—*Action of the Halogens at High Temperatures upon Metallic Oxides.*

By C. F. Cross and S. Sugiura, Students in the Chemical Laboratories of The Owens College.

The action of pure chlorine upon the metallic oxides has already been carefully examined by Weber (*Pogg. Ann.*, cxii, 619), but the behaviour of metallic oxides when treated with bromine and iodine has not been investigated. The following communication contains the results of experiments made with the view of ascertaining the mode and extent of the replacement of the oxygen of the metallic oxides by the halogens when pure and when mixed with air and oxygen.

Lead Oxides.

In the investigation of the action of the halogens upon these oxides two methods were adopted; the oxides were strongly heated (1) in a mixture of the halogen and air, and (2) in the pure halogen. The temperature was regulated so as to avoid the decomposition of the product. The products of the reaction with bromine and chlorine were for the most part liquid at the temperature of the experiment, and the tranquil fusion of the mass was a criterion of the completion of the reaction; to ensure this, however, the crystalline mass formed on cooling was finely powdered, and the operation repeated. The compounds obtained with iodine were heavy infusible powders, and therefore the operation was in each case repeated until the composition of the residue remained constant.

Action of Mixture of Iodine Vapour and Air.

The following are the analyses of the products obtained:—

	From PbO_2. (*a*.)	(*b*.)	From Pb_3O_4.	Calc. $Pb_{11}I_4O_{10}$.*
Pb	77·22	76·88	77·00	77·32
I.....	17·49	17·44	17·14	17·35
O†	5·29	5·68	5·86	5·33
	100·00	100·00	100·00	100·00

Both the above oxides therefore yield the same body; it is an infusible yellow powder, sp. gr. 7·81, from which boiling water abstracts no lead iodide, and in which none of the iodine is present as an oxy-acid.

	From PbO. (*a*.)	(*b*.)	Calc. $Pb_9I_2O_8$.
Pb.....	82·69	—	82·98
I.....	11·68	11·55	11·31
O	5·63	—	5·71
	100·00		100·00

This body is also a heavy yellow powder The atomic ratio of Pb : O approaches that of equality in all the above compounds.

Action of Pure Iodine.

The products of this reaction are orange-yellow infusible powders, having the following composition:—

	From PbO_2.	Calc. $Pb_{11}I_5O_7$.	From PbO.	Calc. $Pb_9I_4O_6$.
Pb ..	74·62	75·30	75·75	75·52
I....	21·28	21·00	20·11	20·59
O ...	4·10	3·70	4·14	3·89
	100·00	100·00	100·00	100·00

The percentage of residual oxygen is less than in the preceding cases, but is also constant; the ratio Pb : O is approximately 3 : 2.

Action of Bromine and Air.

Products, fusible grey powders.

	From Pb_3O_4. (1) A.	(2)	B.	Calc. $Pb_4Br_5O_2$.
Pb....	66·16	66·15	65·54	65·71
Br....	31·68	31·49	32·02	31·74
O	2·16	2·36	2·44	2·55
	100·00	100·00	100·00	100·00

(Ratio Pb : O = 2 : 1.)

* Oxygen in all cases by difference.

† The formulæ given in this paper serve simply to express the results of analysis, and to point out the ratio of halogens to residual oxygen.

	From PbO.* (Mean of analyses of 6 preparations.)	Calc. $Pb_6Br_7O_2$.
Pb	67·17	67·72
Br	30·97	30·53
O.....	1·86	1·75
	100·00	100·00

(Ratio Pb : O = 3 : 1.)

Action of Pure Bromine.

This reaction was marked by the fusion of the products at a comparatively low temperature; in the case of the dioxide a pale brown crystalline mass is obtained, and with the monoxide a yellowish-white crystalline body remains on cooling. The following are the analyses:—

	From PbO_2.	From PbO. (*a.*)	(*b.*)	Calc. $Pb_7Br_{11}O_2$.
Pb....	61·22	61·37	61·01	61·38
Br....	37·31	37·17	37·63	37·27
O	1·47	1·46	1·36	1·35
	100·00	100·00	100·00	100·00

These bodies appear to be identical. As is the case with iodine pure bromine displaces more oxygen than when it is mixed with atmospheric air, and this occurs in nearly the same proportion as is observed with iodine. The ratio Pb : O, which is now 7 : 2, also exhibits a progressive increase.

Action of Chlorine and Air.

In this case also the products are easily fusible and cool to crystalline solids of a greyish colour. The following is the composition of these bodies:—

	From PbO_2. (*a.*)	(*b.*)	Calculated $Pb_{12}Cl_{21}O_4$.	From PbO. (*a.*)	(*b.*)	Calculated $Pb_8Cl_{16}O$.
Pb ..	75·68	75·30	75·55	74·73	74·59	73·94
Cl ..	22·45	22·86	22·51	24·54	24·73	25·35
O ...	1·87	1·84	1·94	0·73	0·68	0·71
	100·00	100·00	100·00	100·00	100·00	100·00
	(Ratio Pb : O = 3 : 1).			(Ratio Pb : O = 8 : 1).		

* This was the only case in which we failed to obtain constant results; the percentages of bromine varied between 29·2 and 31·3.

	From Pb_3O_4.	Calc. Pb_5Cl_9O.
Pb	75·05	75·52
Cl	23·80	23·31
O.....	1·15	1·19
	100·00	100·00

(Ratio Pb : O = 5 : 1).

The ratios of lead to oxygen exhibit a progressive increase. It will be observed that the products obtained from the several oxides differ from one another in composition, being richer in chlorine and less rich in oxygen, according as the original oxide contained a less or greater percentage of oxygen.

Action of Pure Chlorine.

It was observed that the dioxide was not completely decomposed until the temperature reached a red-heat, at which point also the monoxide was completely converted into chloride. The following are the analyses:—

	From PbO_2.	Calc. Pb_4Cl_7O.		From PbO.	Calc. $PbCl_2$.
Pb....	76·67	75·84	Pb....	74·95	74·46
Cl....	21·93	22·74	Cl....	25·63	25·54
O	1·40	1·42			
	100·00	100·00		100·00	100·00

(Ratio Pb : O = 4 : 1).

Finally it was necessary to ascertain whether the percentage of residual oxygen in the products of the action of the mixture of the halogen and air would be increased by substituting for the latter pure oxygen. The monoxide and dioxide were therefore heated in a stream of pure oxygen mixed with the vapour of iodine, the operation being twice repeated. The products of the reaction were yellow powders of the following composition:—

	From PbO.	From PbO_2.	Calc. $Pb_{12}I_5O_{11}$.
Pb.....	75·55	75·34	75·38
I.....	19·03	19·56	19·27
O	5·42	5·10	5·35
	100·00	100·00	100·00

(Ratio Pb : O approximately = 1).

They are therefore identical. On comparing these results with those obtained with a mixture of iodine and air, it is evident that the extent of replacement of oxygen by the halogen in presence of oxygen is independent of the amount of the latter supplied during the reaction.

In conclusion, we would draw attention to the constancy of the percentage of the residual oxygen in the products of each series of reactions, and to the following numbers which express the relations of the several series to one another in this respect:—

	Mean percentage residual oxygen.		
	Pure halogen.	Halogen and air.	Ratio.
I compounds	4·12	5·63	1 : 1·3
Br „	1·43	2·14	1 : 1·5
Cl „	·76	1·25	1 : 1·7

The ratios of lead to oxygen also exhibit a progressive increase which has been already indicated.

Action of Iodine upon the Oxides and Carbonates of the Alkaline Earth-Metals.

The action of iodine in presence of oxygen upon the above compounds is interesting, inasmuch as in place of oxy-iodides, periodates of the metals are formed. Thus lime, exposed at a high temperature to the action of iodine vapour mixed with air, yields basic calcium periodate, but no iodide or oxy-iodide. Barium dioxide and barium carbonate treated in a similar way also form basic barium periodate, but no iodide. The product thus obtained dissolves completely in strong nitric acid without liberation of iodine, which, however, occurs on heating with zinc and hydrochloric acid, whilst on warming with hydrochloric acid chlorine is liberated. A solution giving all the reactions of periodic acid is readily obtained by decomposing the product of the action with sulphuric acid. When oxygen or atmospheric air is replaced by carbon dioxide, no formation of periodate is observed in the case of barium carbonate, whilst the amount produced with barium dioxide is smaller than when oxygen is present, showing that the fixation of iodine by the alkaline earths occurs only in presence of oxygen.

XLIX.—*On Manganese Tetrachloride.*

By W. W. Fisher, M.A., Aldrichian Demonstrator of Chemistry, Oxford.

When binoxide of manganese is treated with cold concentrated hydrochloric acid it dissolves, forming a dark-brown liquid. This liquid evolves chlorine slowly at ordinary temperatures, more quickly when heated, and finally appears almost colourless, and contains only manganous chloride. If the freshly prepared brown solution is diluted

largely with water it remains clear for a few seconds, but presently becoming turbid, deposits a copious brown precipitate, which on analysis proves to be hydrated binoxide of manganese. Moreover, when either the sesquioxide, or the so-called "red oxide" (manganoso-manganic oxide) is similarly treated with hydrochloric acid similar brown solutions are obtained, which give on dilution precipitates of hydrated oxide not distinguishable in appearance from the brown precipitate obtained from the binoxide. Forchammer in 1821 published an account of these phenomena, and thought that the brown liquid contained an unstable sesquichloride of manganese. He states that the precipitated oxides are mixtures.

Nicklès* in 1864 published an account of his experiments on this subject, and showed that by the action of gaseous hydrogen chloride upon binoxide of manganese in dry ether, a green solution is produced which varies indeed in composition, but contains manganese and chlorine in the proportion of Mn : Cl_4 = 55 : 142. From one of his analyses of the green liquid he obtained the formula, $MnCl_2 + 12(C_4H_5O) + 2HO$(Mn = 27·5, C = 6, O = 8).

He further obtained from red oxide of manganese in amylic alcohol a green compound containing excess of hydrochloric acid, to which he assigns the formula $Mn_2Cl_3 + 2(C_{10}H_{12}O_2) + ClH + 8HO$.

In consequence of the ready splitting up of these higher chlorides, their investigation is one of much difficulty; but I have tried to obtain some evidence of the nature of these compounds by decomposing portions of freshly prepared solutions with potassium iodide, as nearly as possible simultaneously, and then at leisure completing the quantitative determinations necessary.

It seemed in the first instance probable that hydrochloric acid treated with an excess of oxide of manganese would be entirely converted into a perchloride, and a determination of the compound formed might be made according to the following equation:—

$$MnCl_{(2+x)} + yKI = MnCl_2 + xKCl + (y - x)KI + I_x,$$

from which the ratio of manganese to free iodine might readily be ascertained.

Pure precipitated binoxide of manganese was treated with an insufficient quantity of hydrogen chloride. The sample of oxide used contained

MnO_2	73·12
MnO	1·01
H_2O	25·93
	100·06

* Mémoires de l'Académie de Stanislas, 1865. Nancy.

The experiments were carried on in May at the ordinary temperature of the laboratory. No freezing mixtures were used in any case. Under these circumstances the alteration in the quantity of chlorine in solution was so rapid and continuous that it was found impossible to obtain a definite material for analysis. The decomposition of the brown solution by water was next tried, and the result proved entirely satisfactory.

If we suppose the action of hydrochloric acid upon manganese dioxide to be represented by equation I :—

$$\text{I. } MnO_2 + 4HCl = MnCl_4 + 2H_2O,$$

it is probable that the decomposition by water is represented by the same equation with the sides reversed in order :—

$$\text{II. } MnCl_4 + 2H_2O = MnO_2 + 4HCl.$$

The oxide and chloride doubtless are both hydrated, but the water cannot be determined. Further, on adding potassium iodide to the original solution, we shall have the decomposition represented by equation III :—

$$\text{III. } MnCl_4 + 2KI = MnCl_2 + 2KCl + I_2,$$

and by comparing equations II and III we see that the manganese precipitated from a defined volume of solution will be related to the iodine liberated from an equal amount of solution in the ratio of $Mn : I_2 = 55 : 254$, which corresponds with $Mn : Cl_2 = 55 : 71$.

With these relations in view experiments were made, but it was discovered that it was necessary to guard against two sources of error :—1st. After the precipitation of oxide of manganese the filtrate contains free chlorine, which must be determined without loss. 2nd. The oxide of manganese thrown down is slowly redissolved by the excess of acid present. To prevent this secondary reaction a quantity of sodium acetate must be added, since the acetic acid thereupon set free is without appreciable action upon the precipitate.

The following method of experimenting was finally adopted as the most convenient and accurate :—

A solution was prepared by digesting one part of manganic oxide with ten parts of strong acid. The exact proportions are unimportant, but excess of acid increases the stability of the manganic chloride. After a few minutes, when the oxide appeared to be dissolved, the dark brown solution was filtered through spun glass and poured into a burette, from which two suitable quantities were immediately run off and treated as follows :—

(A.) A definite volume was delivered into a solution of potassium

iodide. Subsequently, by the use of a standard solution of sodium hyposulphite, the liberated iodine was estimated.

(B.) A definite volume was delivered into a solution of sodium acetate. The brown precipitate of manganic oxide which quickly formed was filtered off, washed, dried, ignited, and weighed as Mn_3O_4. The free chlorine in the filtrate was estimated by treating with potassium iodide and sodium hyposulphite, but to prevent loss a special arrangement was made.

A funnel with a carefully fitted filter-paper, supported by a platinum cone, was fixed in a Woulffe's bottle, which could be exhausted by an air-pump, and the neck of the funnel was drawn out so as to dip beneath the surface of a solution of potassium iodide placed in the bottle. The liquid passing through the paper thus ran directly into the iodide solution and a quantity of iodine, equivalent in amount to the free chlorine, was instantly liberated. As a measure of precaution, to prevent loss of iodine vapour, a U-tube with a little solution of potassium iodide was interposed between the bottle and air-pump. The liquid in this tube, however, acquired only the slightest tinge of colour. The connections of the Woulffe's bottle moreover were of glass ground in air-tight. The top of the funnel during filtration was covered by a watch-glass, and here a small quantity of chlorine was necessarily lost by diffusion into the air, but the loss was not important when the filtration was completed within a few minutes.

From experiment A we get the total iodine set free, and from B we get the manganese and a smaller amount of iodine set free. The difference between the iodine in A and the iodine in B is calculated into chlorine and compared with the manganese.

The following are some of the results obtained:—

I. Mn_3O_4 from 20 c.c. = ·2420 gram.

A. 20 c.c. required ·225·07 c.c. hypo. = ·3517 chlorine.
B. Filtrate „ 75·4 c.c. „ = ·1175 „

II. Mn_3O_4 from 20 c.c. = ·2420 gram.

A. 20 c.c. required 221·85 c.c. hypo. = ·3462 chlorine.
B. Filtrate „ 75· c.c. „ = ·1168 „

From experiment I we have manganese ·1748 gram.
(A—B) chlorine ·2349 „
Free.
or Mn : Cl = 1 : 2·08.

From experiment II we have manganese ·1748 gram.
(A—B) chlorine ·2304 „
Free.
or Mn : Cl = 1 : 2·04.

These results, which were confirmed by many others, it will be seen are perfectly in accordance with the reactions expressed by equations II and III, given above.

Action of Hydrochloric Acid on Sesquioxide of Manganese.

If we suppose the reactions with Mn_2O_3 to take place, thus :—

$$\text{I. } Mn_2O_3 + 6HCl = Mn_2Cl_6 + 3H_2O$$
$$\text{II. } Mn_2Cl_6 + 3H_2O = Mn_2O_3 + 6HCl$$
$$\text{III. } Mn_2Cl_6 + 2KI = 2MnCl_2 + 2KCl + I_2$$

we shall get from equations II and III the ratio :—

$$Mn_2 : I_2 = 55 : 127, \text{ or } Mn_2 : Cl_2 = 55 : 35{\cdot}5.$$

A sample of sesquioxide was prepared by igniting the pure binoxide to low redness. This lost on ignition to bright-red heat 3·85 per cent. of oxygen (theory = 3·97), showing that the product was nearly pure. A small quantity was then dissolved in hydrochloric acid, precipitated by solution of sodium acetate, and dried at 180°. It lost on ignition 13·2 per cent. of oxygen, and would therefore seem to be, *not sesquioxide, but binoxide*, which loses 12·35 per cent. of oxygen.

A volumetric determination was therefore made, the solution being prepared as before :—

Mn_3O_4 found	= ·2765 gram in 10 c.c.
Chlorine found (A)	= 160·6 hypo.
„ „ (B)	= 17·6 „
Difference	143·0 „
Whence chlorine	= ·2444 gram
manganese	= ·2508 „
or Mn : Cl	= 1 : 2·02.

A result identical with that obtained from binoxide of manganese.

Action of Hydrochloric Acid upon Red Oxide of Manganese.

A sample of pure red oxide (Mn_3O_4), and also the dioxide used in these experiments, was obtained from Messrs. Hopkin and Williams. It was analysed with the following result :—·2750 gram lost at 180° ·0035 water, and lost no appreciable weight when afterwards ignited. It is substantially pure.

When dissolved in hydrochloric acid and reprecipitated with solution of sodium acetate, an oxide was obtained which, after being dried at 180°, lost on ignition 12·4 per cent. of oxygen. This oxide is therefore also binoxide, which loses 12·3 per cent. of oxygen.

Determinations were then made by the volumetric method.

I. Mn_3O_4 found from 10 c.c. = ·074.

Chlorine found (A) = 48·3 c.c. hypo.
„ „ (B) = 7·5 „ „

Difference .... 40·8 „ „
Hence chlorine = ·0708 gram
manganese = ·0533 „
or Mn : Cl = 1 : 2·07.

II. Mn_3O_4 from 10 c.c. = ·074.

Chlorine found (A) = 47·0 c.c. hypo.
„ „ (B) = 7·5 „ „

39·5 „ „
Hence chlorine = ·0689 gram
manganese = ·0533 „
or Mn : Cl = 1 : 2·003,

which is also identical with the result obtained from binoxide of manganese.

We find therefore from these experiments that the oxides of manganese higher in degree than the protoxide, when treated with excess of strong hydrochloric acid, give brown liquids containing a highly chlorinated manganese-compound, which is easily resolved into manganous chloride and free chlorine, and that on dilution with water *manganese binoxide* in a hydrated condition is precipitated in each instance. The solutions obtained seem to have identical properties, and it is in the highest degree probable that the same compound, $MnCl_4$, is formed in each.

Under the conditions of the experiment the intermediate chlorides, Mn_2Cl_6 and Mn_3Cl_8, do not appear to be formed directly from the corresponding oxides, nor do they appear as products of a partial dechlorination of the tetrachloride. This conclusion is supported by the experiments of Nicklès, who obtained in fact from the higher oxide compounds containing the higher chloride, but from the lower oxide green liquids containing only chlorides of indefinite composition. His formula, $Mn_2Cl_3 + HCl + 2(C_{10}H_{12}O_2) + 8HO$, might very possibly be $Mn_2Cl_4 + 2(C_{10}H_{12}O_2) + 8HO$, which would agree equally well with the results of analysis.

The action upon the two oxides may be represented by the equations—

$$Mn_3O_4 + 8HCl = 2MnCl_2 + MnCl_4 + 4H_2O$$
$$Mn_2O_3 + 6HCl = MnCl_2 + MnCl_4 + 3H_2O,$$

but since a large excess of hydrochloric acid or alkaline chlorides is found to render manganese tetrachloride comparatively more stable,

it is probable that this body exists only in combination in a form analogous to chloroplatinic acid. I am occupied with experiments in support of this view, and hope shortly to bring the results before the Society.

I wish to acknowledge the kind assistance of Mr. V. H. Veley, of University College, in carrying out most of the experimental work connected with this investigation.

L.—*Contributions to the History of the Naphthalene Series.* No. II. *β-Naphthaquinone.*

By John Stenhouse, LL.D., F.R.S., and Charles E. Groves.

β-Napthaquinone.

In a paper communicated to the Chemical Society last year (1877, ii, 47), we mentioned that nitroso-β-naphthol, when converted into the corresponding amido-naphthol, and then submitted to oxidation, yielded a crystalline compound of the nature of a quinone; this we designated β-naphthaquinone, in order to distinguish it from the α-naphthaquinone previously described by one of us. Further experience has shown us that in preparing this quinone it is more advantageous to employ a considerably larger quantity of potassium dichromate than that formerly used. The proportions which we recommend are 6 parts of a saturated aqueous solution of sulphurous acid, 6 of dilute sulphuric acid (1 vol. acid to 2 of water), and 3 of potassium dichromate to every 2 parts of the pure nitroso-β-naphthol, the reduction and subsequent oxidation being carried out in the manner previously described (*loc. cit.*, 52). In this way the nitroso-naphthol yields from 62—65 per cent. of its weight of the pure quinone, the theoretical quantity being 91·9. We have not ascertained the cause of this deficiency, but as the sulphur precipitated during the reduction of the nitroso- to the amido-compounds contains but very little organic matter, it is probable that the loss is occasioned chiefly by the solution of a portion of the amido-β-naphthol in the dilute solution of ammonium sulphide. This solution, however, after it has been acidified with sulphuric acid, and the hydrogen sulphide removed by heating, does not yield any quinone when mixed with a solution of potassium dichromate, as it should do if there were any quantity of the amido-naphthol present.

University of Michigan

Nitro-β-naphthaquinone.

It was noticed that β-naphthaquinone dissolved readily in hot dilute nitric acid, and the solution on cooling deposited a crystalline substance of a magnificent crimson colour. Since our last communication we have prepared this substance in a state of purity. The pure β-quinone (10 parts) was added to nitric acid of density 1·2 (60 parts by measure), and after the mixture had been agitated until it formed a homogeneous paste, the flask was plunged into boiling water. The quinone dissolved, and in the course of a few minutes a mass of red crystals of the new substance separated, a small quantity of nitrous fumes being at the same time evolved; this was no doubt due to secondary action. When the whole of the quinone was converted into the nitro-derivative, which only required a few minutes, the flask was removed from the water-bath and plunged into cold water, so as to stop the oxidising action of the hot nitric acid on the nitroquinone. After allowing it to stand for a couple of hours, the product was collected and washed, first with a little dilute nitric acid (density 1·2), and then with water. The crude product amounted to 70—75 per cent. of the naphthaquinone originally taken; it was purified by dissolving it in 15 times it weight of boiling benzene, and allowing the solution to stand for 18 to 24 hours, as it separated but slowly. The hard crimson nodules which formed on the sides of the flask were finally crystallised once or twice from twice their weight of boiling glacial acetic acid, which on cooling deposited the nitro-β-naphthaquinone in magnificent crimson plates, bearing a striking resemblance in point of colour and general aspect to chromic anhydride.

It gave the following results on analysis:—

I. ·301 gram of substance gave ·654 gram carbonic anhydride and ·075 gram water.

II. ·197 gram of substance gave ·429 gram carbonic anhydride and ·046 gram water.

III. ·427 gram of substance gave 25·4 cub. cent. of nitrogen at 18·5° c., and under a barometric pressure of 764·8 mm. (corr. at 0°) equivalent to 23·443 cub. cent. dry nitrogen at 0°, or ·029408 gram of nitrogen.

IV. ·364 gram of substance gave 21·5 cub. cent. of nitrogen at 17·5°, and under a barometric pressure of 745·9° mm. (corr. at 0°) equivalent to 19·830 cub. cent. dry nitrogen at 0°, or ·024877 gram of nitrogen:—

				I.	II.	III.	IV.	Mean.
C_{10}	=	120	59·11	59·26	59·39	—	—	59·32
H_5	=	5	2·46	2·77	2·59	—	—	2·68
N	=	14	6·90	—	—	6·89	6·83	6·86
O_4	=	64	31·53	—	—	—	—	—
		203	100·00					

These numbers correspond with the formula for *mononitro-β-naphthaquinone*, $C_{10}H_5(NO_2)O_2$. It has been already shown (*loc. cit.*) that this substance yields phthalic acid on oxidation, so that both the NO_2 group and the two oxygens of the quinone must be in one and the same benzene ring (adopting Graebe's graphic formula for naphthalene), but nothing is known of their relative positions. It is not unlikely, however, if the β-quinone should really prove to be a meta-derivative, that the nitro-quinone will be found to be $O : O : NO_2 = 1 : 3 : 4$; but at present so little is known of the order in which the hydrogen-atoms are displaced in naphthalene, that this must be regarded as purely hypothetical.

Nitro-β-naphthaquinone is insoluble in light petroleum, almost insoluble in carbon bisulphide, slightly soluble in ether, more so in benzene and in boiling alcohol, and very readily soluble in hot glacial acetic acid; boiling with alcohol, however, appears to decompose it, as the substance does not crystallise out again as the solution cools, and on evaporation it merely deposits yellow oily drops. It dissolves pretty freely also in boiling acetic acid of 30 per cent. (density 1·04), and to a less extent in water; the orange-coloured solutions become opalescent on cooling, but do not yield crystals. It is soluble in concentrated sulphuric acid in the cold, but is at the same time decomposed, the dark-coloured liquid giving a brown precipitate when diluted with water. The nitroquinone melts at 158°, and when strongly heated on platinum foil burns with feeble deflagration. It undergoes reduction when treated with hydriodic acid and phosphorus, with formation of two compounds, probably the corresponding nitrohydroquinone and the amidohydroquinone, crystallising in large crimson plates and in red-brown needles; these new substances have not as yet been further examined. Aqueous solution of sulphurous acid also reduces the nitroquinone.

Dinaphthyldiquinhydrone.

It had been noticed in the preparation of β-naphthaquinone that if the freshly precipitated quinone was allowed to stand for any length of time in contact with the acid solution, it lost its bright orange colour, and became darker; this at the time was attributed to oxi-

dation by the excess of potassic dichromate employed for its precipitation, but we have since ascertained that it is due to another cause. When the quinone is heated with mineral acids, or even when it is left in contact with them in the cold for a sufficient length of time, it is converted into a compound of a purplish-black colour analogous to quinhydrone: it is to the formation of this substance by the action of the free sulphuric acid, that the darkening of the naphthaquinone just mentioned is due, and not to oxidation.

The most convenient agent for the transformation of the β-naphthaquinone was found to be dilute sulphuric acid (1 vol. of acid to 2 of water). When the pure quinone (1 part) was intimately mixed with the acid (10 parts by measure), so as not to leave any portion unwetted, and allowed to stand for 24 hours, it was completely converted into the black substance, or the change could be more rapidly and conveniently effected by heating the mixture in a water-bath at about 55°; the quinone rapidly became dark-coloured, and at the end of ten minutes the reaction was complete. If the temperature was allowed to rise much above 60° soft pasty masses were formed inclosing some of the unaltered β-quinone, so that it became somewhat difficult to convert the quinone entirely into the new compound. About twice its bulk of water was added to the mixture when cold, and the product collected and thoroughly washed with cold water to free it from adhering sulphuric acid.

The diquinhydrone thus prepared forms an indigo-black powder when dry, which is insoluble in water, carbon bisulphide, and light petroleum, almost insoluble in benzene, but soluble in glacial acetic acid; the reddish-brown solution is immediately decolorised on addition of sulphurous acid solution. The diquinhydrone dissolves in concentrated sulphuric acid with production of a deep green colour; the addition of water to this solution produces a precipitate.

Treated with reducing agents, such as hydriodic acid and phosphorus, or an aqueous solution of sulphurous acid, the diquinhydrone is converted into a colourless substance crystallising in needles, whilst with oxidising agents, as nitric acid or potassium dichromate and sulphuric acid, it yields orange-coloured prisms, so that these three substances stand in the same relation to one another as do green quinhydrone, quinol or hydroquinone, and quinone, in the benzene series.

Dinaphthyldiquinone.

The quinhydrone just described is easily converted into dinaphthyldiquinone by boiling it with nitric acid, or with a solution of potassium dichromate and sulphuric acid, but it is more conveniently prepared by pouring a solution of pure dinaphthyldiquinol in boiling 30 per cent.

acetic acid, into nitric acid (density 1·45) in quantity sufficient to oxidise the hydroquinone. In this way the diquinone is precipitated in small lustrous prisms of a brilliant orange colour. If, however, the nitric acid be added to the acetic acid solution, instead of pouring the latter on to the nitric acid, the precipitate is of a dingy colour, probably owing to the presence of a small quantity of the diquinhydrone.

The following results were obtained on analysis of this substance dried at 100°:—

I. ·196 gram substance gave ·549 gram carbonic anhydride and ·061 gram water.

II. ·104 gram substance gave ·2915 gram carbonic anhydride and ·033 gram water.

III. ·261 gram substance gave ·732 gram carbonic anhydride and ·082 gram water.

				I.	II.	III.	Mean.
C_{10}	=	120	76·43	76·39	76·44	76·49	76·44
H_5	=	5	3·18	3·46	3·52	3·49	3·49
O_2	=	32	20·39	—	—	—	—
		157	100·00				

The analytical numbers agree with the empirical formula, $C_{10}H_5O_2$; but from a consideration of the mode of formation this should be doubled, making the formula of the dinaphthyldiquinone $C_{20}H_{10}O_4$.

Dinaphthyldiquinone is insoluble in water, and but very slightly soluble, or quite insoluble, in all ordinary solvents; even boiling glacial acetic acid dissolves it but very sparingly. The diquinone is a very stable body, dissolving in boiling concentrated nitric acid, and crystallising out unchanged on cooling; by long continued boiling with the acid, however, it appears to be decomposed, and it is not improbable that a study of the products of oxidation formed in this way will yield interesting results. It is also easily soluble in warm concentrated sulphuric acid, and is precipitated again on dilution. Reducing agents convert it into the corresponding hydroquinone.

Dinaphthyldiquinol.

This compound is formed by the reduction of the diquinone or diquinhydrone, as when they are boiled with phosphorus and a solution of hydriodic acid in acetic acid of 30 per cent., or treated with aqueous solution of sulphurous acid; the quinone, however, appears to be more easily reduced than the quinhydrone. The diquinone, when allowed to stand for some time in contact with sulphurous acid solution, becomes converted into a mass of colourless crystals of the

diquinol; the quinhydrone does not appear to be produced as an intermediate stage in this reaction, for at no time could the black crystals of this compound be distinguished in the mixture. A very convenient method of preparation is to convert the β-naphthaquinone into the diquinhydrone by treatment with dilute sulphuric acid in the manner previously described, and when the mixture is cold, to add about twice its bulk of a saturated aqueous solution of sulphurous acid, and allow the whole to stand for 24 hours, when the black diquinhydrone will be found to be entirely converted into a mass of snow-white needles of dinaphthyldiquinol, provided the β-naphthaquinone originally employed was quite pure: these merely require to be thoroughly washed to remove sulphuric acid, and crystallised once from dilute acetic acid, to which a few drops of sulphurous acid solution have been added, to be quite pure. If impure β-quinone has been used for the preparation of the diquinhydrone, the diquinol will be coloured and somewhat difficult to purify; repeated conversion into the diquinone and reconversion into the diquinol will, however, usually suffice to render it colourless.

Dinaphthyldiquinol, $C_{20}H_{14}O_4$, or $C_{20}H_{10}(OH)_4$, forms colourless needles, which, on drying, become darkened from partial oxidation. It melts at 176—178°, is almost insoluble in water, moderately soluble in 30 per cent. acetic acid, easily in the glacial acid. It is only slightly soluble in benzene, bisulphide of carbon, and ether. The analytical results were as follows:—I. ·244 gram substance, gave ·676 gram carbonic anhydride and ·0905 gram water.

C_{20}	= 240	75·47	75·56
H_{14}	= 14	4·40	4·12
O_4	= 64	20·13	—
	318	100·00	

These numbers show a deficiency in hydrogen for the formula, $C_{20}H_{14}O_4$, which is what might be expected from the comparative ease with which the substance becomes oxidised.

Mode of Formation of Dinaphthyldiquinhydrone.

The conversion of β-naphthaquinone into the black diquinhydrone, under the influence of acids, would seem to take place by the condensation of 2 molecules of the quinone, with elimination of two atoms of hydrogen which unite with two out of the four oxygen atoms in the double quinone-molecule to form a quinhydrone—

$$C_{10}H_6O_2 + C_{10}H_6O_2 = C_{20}H_{10}O_2(OH)_2,$$

or regarding the quinhydrone as formed by the union of a molecule of the quinone with one of the quinol:

$$2C_{10}H_6O_2 + 2C_{10}H_6O_2 = C_{20}H_{10}O_4.C_{20}H_{10}(OH)_4.$$

This view is strongly supported by the fact that β-naphthaquinone yields its own weight of the diquinhydrone. Two experiments were made, in each of which ·500 gram of pure β-naphthaquinone was converted into the diquinhydrone by treatment with dilute sulphuric acid: the products collected, washed thoroughly, and dried, weighed ·498 and ·495 gram respectively.

It was evident that the results of an analysis of the diquinhydrone for hydrogen (taking into consideration its high molecular weight, and that in all probability it readily alters by oxidation) would not yield satisfactory evidence as to whether this is a correct explanation of the change which takes place. It seemed probable, however, that if the hydrogen-atoms external to the nucleus (that is, those not directly attached to carbon-atoms) could be determined, it would at once show whether the reaction was of the nature above indicated: a means of doing this is afforded by the action of bromine in aqueous solution, which readily oxidises the diquinhydrone, but does not attack the diquinone. A weighed quantity of the pure β-naphthaquinone was accordingly converted into the black diquinhydrone, and agitated with excess of bromine-water of known strength for a few minutes, whereby it was converted into the diquinone; the excess of bromine was then estimated by potassic iodide and hyposulphate solution in the usual manner. In this way it was found in two experiments that ·200 gram of pure β-naphthaquinone, after conversion into the diquinhydrone, required ·100 and ·098 of bromine respectively to oxidise it to the new quinone; the theoretical amount for

$$C_{20}H_{10}O_2(OH)_2 + Br_2 = C_{20}H_{10}O_4 + 2HBr$$

being ·101 gram bromine. There can be little doubt, therefore, that the black substance is a diquinhydrone analogous to the green quinhydrone of the benzene series.

Although it was almost certain—the nature of the diquinone and diquinhydrone being established—that the formula of the diquinol was $C_{20}H_{10}(OH)_4$, notwithstanding the analytical results showed a deficiency in the hydrogen; yet it was thought advisable to make experiments by oxidation with bromine-water in a manner similar to those detailed for the diquinhydrone, with a view to ascertain whether it actually contained four OH-groups. From the readiness with which the substance oxidises, however, the results were not very accordant. A weighed quantity of the dinaphthyldiquinone, $C_{20}H_{10}O_4$, was reduced by sulphurous acid solution, washed thoroughly, collected on a vacuum

filter, and the product, which had already become slightly coloured, was dissolved in hot glacial acetic acid; the rather dark-coloured solution was then poured into an excess of bromine-water, and the excess of free bromine determined as before. Three experiments gave 98 : 88·5 and 85 of bromine per 100 of the diquinone, whilst theory requires 101·9. The diquinone formed in these oxidation experiments was examined, to ascertain if any bromine substitution-derivative had been formed, but it was found to be free from bromine.

The compound, $C_{20}H_{10}(OH)_4$, may be regarded as a tetrahydric alcohol of the hydroquinone or quinol species, derived from a dinaphthyl, $C_{10}H_7.C_{10}H_7$, by the displacement of four hydrogen-atoms by four OH-groups, and is a member of a new class of bodies, the *diquinols*. We have, therefore, called it *dinaphthyldiquinol*, and the corresponding quinone-compound, *dinaphthyldiquinone*.

We have ascertained that benzoquinone and α-naphthaquinone also yield diquinones and diquinols by condensation, and have no doubt that other quinones will yield corresponding compounds. We are at present engaged in studying this interesting group.

Our thanks are due to Mr. F. Sear for the care with which he has done much of the analytical work in connection with this paper.

LI.—*Notes on Madder Colouring Matters.* (Continuation.)

By Edward Schunck, Ph.D., F.R.S., and Hermann Roemer, Ph.D.

6. Identity of Purpuroxanthic Acid and Munjistin.

In order to remove any remaining doubt as to the identity of the colouring matter obtained by us from commercial purpurin with the munjistin of Stenhouse, we prepared a quantity of the latter substance, employing, with merely slight modifications, the process given by the discoverer. One part of ground munjeet was treated with a boiling solution of one part of aluminium sulphate in fifteen parts of water, the treatment being repeated four or five times. The red decoction, after straining through calico, was mixed with hydrochloric acid, which gave a yellow precipitate. This precipitate was treated with boiling concentrated hydrochloric acid, in order to remove the alumina still contained in it; and after being filtered off and well washed with water, it was exhausted with boiling alcohol. The latter removed all the colouring matter of the precipitate, leaving a quantity

of pectic acid and other impurities undissolved. The liquid left after the alcohol had been distilled off a bulky reddish-yellow mass, consisting for the most part of munjistin and purpurin. The two substances were separated by treatment with boiling water, slightly acidified with acetic acid, in which the munjistin dissolved. The filtered liquid gave, on addition of hydrochloric acid, an orange-coloured precipitate, which was filtered off and dissolved in boiling glacial acetic acid. This solution deposited, on cooling, golden-yellow scales of munjistin, small quantities of purpurin and other substances remaining in the mother-liquor. The munjistin was recrystallised from glacial acetic acid until the product melted exactly at 231°. It had the properties of purpuroxanthic acid, and also the same composition, as the following analysis shows:—

0·3454 gram of substance gave 0·8002 gram of CO_2, and 0·0980 gram H_2O.

In 100 parts:

C	63·18
H	3·15

The formula, $C_{14}H_7(COOH)O_4$, requires—

C	63·38
H	2·82

The residue obtained, on evaporating the mother-liquor of the munjistin, contained, beside purpurin, small quantities of alizarin and other bodies. The alizarin was easily detected by employing the method described by us in Note 1.

Although we obtained a much larger quantity of munjistin from munjeet than from commercial purpurin, still in the former, as well as in the latter product, purpurin largely preponderates. The yield from 100 lbs. of munjeet was so considerable that we were able to subject the munjistin obtained to more minute examination.

Its composition, being that of a dioxyanthraquinone-carbonic acid, rendered a study of its derivatives of some interest, more especially as we hoped thereby to arrive at some means of preparing this and similar compounds synthetically. The question arose, whether the decomposition into purpuroxanthin and CO_2, which, as we have shown, is effected quantitatively at 233°, would take place even at a lower temperature, when the substance is exposed to the action of bromine and other reagents. It seemed also of importance to determine whether, by the action of acetic anhydride, the one hydrogen of the carboxyl-group, as well as the two atoms of the hydroxyl-groups, could be replaced by acetyl.

7. Experiments on Munjistin.

Action of Acetic Anhydride on Munjistin.

At the temperature of ebullition, acetic anhydride acts on the substance, yielding a product very easily soluble in the liquid. On the addition of water, a pale yellow mass is precipitated, which melts at about 160°. The compound is, however, unstable. By the action of boiling alcohol or glacial acetic acid, it is reconverted into munjistin. The same compound is formed on heating with acetic anhydride from 160 to 200°. It crystallises from ether in small needles. Its uncertain melting point and its general character show, however, that it is not a pure substance, but a mixture of an acetyl-compound with uncombined munjistin.

Action of Bromine on Munjistin.

On adding to a solution of munjistin in glacial acetic acid, heated to near the boiling point, an excess of bromine, the solution deposits, on cooling, large lustrous prismatic needles of an orange-yellow colour. The product, after crystallisation from glacial acetic acid, in which it dissolves with some difficulty, has a constant melting point of 231°. The same product is obtained when alcohol is used as a solvent instead of glacial acetic acid, but in this case the crystals are much smaller, less lustrous, and of a pure yellow colour. The compound dissolves in alkali, with a reddish-yellow colour. A bromine determination led to the following result:—

0·2542 gram substance yielded 0·2400 gram AgBr, equivalent to 40·17 per cent. of bromine.

Hence it follows that the compound was dibromopurpuroxanthin. The latter contains 40·20 per cent. of bromine, whereas dibromomunjistin would contain 36·19. According to Plath (*Deut. Chem. Ges. Ber.*, ix, 1204), dibromopurpuroxanthin melts at 227—230°). There can be no doubt, therefore, that by the action of bromine on munjistin, the carboxyl-group had been eliminated, and that the bromine-compound of purpuroxanthin had been formed.

Action of Potassic Hydrate on Munjistin.

At the ordinary temperature, a concentrated solution of potassic hydrate does not act on munjistin, but, on boiling, purpurin is formed, as we have already observed.

Action of Ammonia on Munjistin.

Ammonia converts munjistin at the ordinary temperature, though slowly, into purpurinamide. The change is effected easily and com-

pletely by heating to 100°. The product was recognised as purpurinamide by the fine purple colour of its solutions in alcohol, alkalis, and baryta-water, by the peculiar green fluorescence of the alcoholic solution, and by the absorption-bands shown by the barytic solution.

Action of Nitric Acid on Munjistin.

Fuming nitric acid dissolves munjistin after some time. The solution is red, and deposits on further standing long orange-coloured needles. These needles melt at 251°, at the same time giving off much gas. They dissolve in boiling water with a yellow colour, and yield an insoluble crimson barium compound. As the substance very closely resembled the dinitropurpuroxanthin described by Plath, both as regards the melting point, that of dinitropurpuroxanthin being at 249—250°, and other properties, we prepared the nitro-compound of purpuroxanthin and compared it with the substance obtained from munjistin. We found them to be very similar. They are readily distinguished, however, by their behaviour to ammonium acetate, a boiling solution of which dissolves dinitropurpuroxanthin without much difficulty, yielding on cooling an ammonium salt in long, silky needles; whereas the nitro-compound of munjistin dissolves with great difficulty in ammonium acetate, giving a salt in microscopic needles.

LII.—*On Pyrotritartaric and Carbopyrotritartaric Acids, Products of the Action of Dilute Sulphuric Acid on Diacetosuccinic Ether.*

By George H. U. Harrow, Ph.D.

It has been shown that in the action of alkaline hydrates on ethyl acetoacetate, or on substituted derivatives of the same, the decomposition consists in the formation, on the one hand, of a ketone, alcohol and carbon dioxide, and on the other of a substituted acetic acid by the splitting off of the acetyl group, thus:—

$$\begin{array}{l} CO.CH_3 \\ | \\ CXY \\ | \\ COOC_2H_5 \end{array} + OH_2 = \begin{array}{l} CO.CH_3 \\ | \\ CHXY \end{array} + CO_2 + C_2H_6O.$$

$$\begin{array}{l} CO.CH_3 \\ | \\ CXY \\ | \\ COOC_2H_5 \end{array} + OH_2 = \begin{array}{l} CH_2 \\ | \\ COOH \end{array} + \begin{array}{l} CHXY \\ | \\ COOC_2H_5 \end{array}$$

At the suggestion of Professor Wislicenus, I undertook the investigation of the action of dehydrating agents on ethyl diacetosuccinate, a substance which Rugheimer (*Ber.*, vii, 892) prepared by the action of iodine on ethyl acetosodacetate:—

$$2\begin{array}{l} CO.CH_3 \\ | \\ CHNa \\ | \\ COOC_2H_5 \end{array} + I_2 = \begin{array}{l} CO.CH_3 \quad CO.CH_3 \\ | \qquad\qquad | \\ CH\text{———}CH \\ | \qquad\qquad | \\ COOC_2H_5 \quad COOC_2H_5 \end{array} + 2NaI.$$

If the reaction took place in the normal manner, the production of a double ketone was to be expected, thus:—

$$\begin{array}{l} CO.CH_3 \quad CO.CH_3 \\ | \qquad\qquad | \\ CH\text{———}CH \\ | \qquad\qquad | \\ COOC_2H_5 \quad COOC_2H_5 \end{array} + 2OH_2 = \begin{array}{l} CH_3 \quad CH_3 \\ | \qquad | \\ CO \quad\ CO \\ | \qquad | \\ CH_2\text{—}CH_2 \end{array} + 2C_2H_6O + 2CO_2.$$

On boiling ethyl diacetosuccinate with dilute sulphuric acid, however, it was found that the above reaction did not take place, but that the products were an acid of the empirical formula, $C_8H_8O_5$, and the ethyl salt of an acid $C_7H_8O_3$, first prepared by Wislicenus and Stadnicki (*Ann. Chem. Pharm.*, cxlvi, 306) by the dry distillation of tartaric acid, and called by them *pyrotritartaric acid*, and afterwards obtained by Böttinger (*Deut. Chem. Ges. Ber.*, vi, 893) by heating pyruvic acid in sealed tubes with water alone, or with an aqueous solution of barium hydroxide (*ibid.*, viii, 1583) for three days in a flask connected with an inverted condenser. Böttinger called his acid *uvic acid*. The acid $C_8H_8O_5$, which, at Professor Wislicenus's suggestion, I have named "*carbopyrotritartaric acid*," does not appear to have been made previously.

Preparation of Solid Ethyl Acetosodacetate.

Conrad and Limpach (*Ann. Chem.*, cxcii, 153) have recently described an easy and rapid method of making this compound by simply adding ethyl acetoacetate to an alcoholic solution of sodium ethylate. In preparing ethyl diacetosuccinate, however, it is necessary to have the sodium compound in the solid state, and as free as possible from alcohol. The method I employed to obtain it in this state is as follows:—

Ten grams of sodium were dissolved in 100 grams of absolute alcohol; when cold the crystalline mass was mixed with an equal volume of dry ether, and the calculated quantity, 56·5 grams, of ethyl-acetoacetate, also diluted with its own volume of ether, added gradually.

On adding a small quantity of water (about 2 c.c.) and stirring well, ethyl acetosodacetate is precipitated in the crystalline form, and finally the whole becomes almost solid.

The precipitated substance was pressed to remove alcohol and ether, and placed under the air-pump over sulphuric acid until quite dry. The pressed-out liquors furnish a further quantity of sodium compound, soon becoming solid.

The precipitation of ethyl acetosodethacetate, $\begin{matrix} CNa(C_2H_5)(CO.CH_3) \\ | \\ COOC_2H_5 \end{matrix}$, by means of water has also been tried, and succeeds perfectly, the precipitate consisting of fine white silky needles. It may be purified by washing with dry ether and finally dried under the air-pump.

Much more sodium-compound is obtained by precipitation with water than by the simple addition of ether, as formerly practised; indeed, from the ethyl acetosodacetate prepared by Conrad and Limpach's method nothing is precipitated by ether alone.

Preparation of Ethyl Diacetosuccinate.

Finely powdered ethyl acetosodacetate was mixed with sufficient ether to form a thin paste, and an ethereal solution of iodine added, with continual shaking, until sodium iodide ceased to be precipitated, and the liquid became slightly coloured. A small excess of iodine-solution was then added and the whole left to itself for some hours. The ethereal solution was filtered from the sodium iodide and shaken with mercury to remove iodine, filtered, most of the ether distilled off, and the residue placed in dishes to crystallise. The substance, freed from the adhering brown mother-liquor on a vacuum-filter and washed with a little ether, was almost pure ethyl diacetosuccinate. The mother-liquor, on evaporation of the ether, furnished another crop of crystals.

Dry ether was used and the amount of decomposition resulting from the heating during distillation was comparatively small. Mercury was employed instead of soda to remove iodine, in order to avoid the introduction of water, which might have proved detrimental in the subsequent distillation.

The substance so obtained was perfectly white and crystalline, and melted at 78—79°.

·1551 gram gave on combustion ·3150 CO_2 and ·0943 OH_2.

		Theory $C_{12}H_{18}O_6$.	Found.
C	=	55·81	55·39
H	=	6·98	6·75
O	=	37·21	—

Action of Dilute Sulphuric Acid on Ethyl Diacetosuccinate.

Portions of 20 grams of ethyl diacetosuccinate were boiled with 150 grams dilute sulphuric acid (1 to 10) in a flask connected with an inverted condenser. On passing the evolved gas through baryta-water, a precipitate of barium carbonate was formed, showing that *carbon dioxide* is a product of the reaction. A quantitative experiment made by passing the dried gas over soda-lime, showed that the amount formed is equal to about 5 per cent. of the ethyl diacetosuccinate employed.

The boiling was continued until gas ceased to be evolved, which usually happened with the above quantities in about six hours. On cooling, a white crystalline body separated out, mixed with an oil having a strong anise-like odour. On submitting the whole to distillation in steam, the oil passed over with the watery distillate; the latter was re-distilled, and the first portions treated with potassium carbonate; a layer then separated which was dried with potassium carbonate and distilled. It boiled on re-distillation at 78—79°, burnt with a pale-blue flame, and had the burning taste and characteristic odour of *alcohol*.

The Oily Distillate.—Dried with calcium chloride, and fractionally distilled, by far the largest portion of the distillate boiled, with little or no decomposition, at 207—210°, and this, on re-distillation, boiled at 208—209°. The analyses of the substance point to the formula $C_9H_{12}O_3$.

I. ·2067 gram gave ·4830 gram CO_2 and ·1304 OH_2.

II. ·1144 gram gave ·2657 gram CO_2 and ·0752 OH_2.

		Theory $C_9H_{12}O_3$.	I.	II.
C	=	64·28	63·72	63·34
H	=	7·14	7·01	7·30
O	=	28·58	—	—

Pyrotritartaric or Uvic Acid.—On boiling the above-mentioned oil with sodium hydroxide solution for two hours, it was completely converted into alcohol and an acid having the empirical formula $C_7H_8O_3$, identical with the pyrotritartaric acid of Wislicenus and Stadnicki and with Böttinger's uvic acid.

On adding dilute sulphuric acid to the alkaline solution, the pyrotritartaric acid was precipitated in the crystalline form and of a slightly yellow colour.

It was found to be soluble in a considerable quantity of boiling water, almost insoluble in cold water, but soluble in ether, from which solvent it crystallises in prismatic needles. It was repeatedly crystallised from ether in order to purify it. When pure it is perfectly colourless and melts at 135°. Wislicenus and Stadnicki give the melting point of pyrotritartaric acid as 134·5°, and Böttinger that of resublimed uvic acid as 134°. It is volatile in steam, and sublimable without decomposition at temperatures considerably below its melting point, beginning to sublime between 100° and 110°. The crystals obtained by sublimation are long thin prisms upon which smaller crystals group themselves.

On treating a very small quantity of the acid on a watch-glass with two drops of fuming hydrochloric acid and warming slightly, then adding about six drops of strong sulphuric acid, and again gently warming, a fine cherry-red colour makes its appearance. This test was tried with pyrotritartaric acid kindly given me by Professor Wislicenus, and the same red colour was obtained. In applying the test, it is important to add sufficient sulphuric acid, and not to heat too strongly. The reaction does not take place with either sulphuric or hydrochloric acid alone.

Recrystallised from ether the acid gave the following numbers on combustion :—

I. ·1227 gram acid gave ·2675 gram CO_2 and ·0634 gram OH_2.
II. ·1057 gram acid gave ·2323 gram CO_2 and ·0578 gram OH_2.
III. ·1276 gram acid gave ·2791 gram CO_2 and ·0711 gram OH_2.

		Theory $C_7H_8O_3$.	I.	II.	III.
C	=	60·00	59·45	59·93	59·65
H	=	5·71	5·74	6·08	6·19
O	=	34·29	—	—	—

Silver Pyrotritartrate.—This salt was prepared by adding silver nitrate to a solution of the sodium salt formed by neutralising the free acid with sodium carbonate. It is a bulky precipitate which, when heated in the water-bath, or on standing, becomes crystalline. It is soluble in a considerable quantity of boiling water with only very slight decomposition, and was in fact purified by crystallisation from water; from very dilute solutions it crystallises in rosette-shaped groups of needles. It becomes yellowish when exposed to light in the dry state. On analysis the following numbers were obtained :—

I. ·102 gram salt gave ·1247 CO_2, ·0312 OH_2, and ·0432 Ag.
II. ·0655 gram salt gave ·081 CO_2, ·0298 OH_2, and ·0276 Ag.

		Theory $C_7H_7AgO_3$.	I.	II.
C	=	34·01	33·34	33·73
H	=	2·83	3·39	3·53
Ag	=	43·73	42·35	42·13
O	=	19·43	—	—

The low percentage of silver in the combustions is due to a portion of the silver being volatilised, the combustion tube being coloured yellow by the silver. The silver was determined by heating the salt very gradually in a porcelain crucible.

		Theory.
I.	·1491 gram salt gave ·0651 gram Ag = 43·66	43·7
II.	·1656 gram salt gave ·0714 gram Ag = 43·12	—
III.	·1124 gram salt gave ·0484 gram Ag = 43·06	—

On heating the silver salt, the sides and lid of the crucible became covered with a crystalline sublimate, which was shown by its melting point, 135—136°, to be pyrotritartaric acid.

Sodium Pyrotritartrate.—Pyrotritartaric acid was neutralised with sodium carbonate, the solution evaporated to dryness on the water-bath, and the organic salt extracted with absolute alcohol, the alcohol evaporated off, and the white crystalline residue dissolved in water, in which it is easily soluble, and evaporated.

·1914 gram of the air-dried salt lost ·0348 gram on heating to 100° = 18·18 per cent. OH_2; theory, $C_7H_7NaO_3 + 2Aq$ requires 18·18 per cent. OH_2.

·1566 of salt dried at 100° gave ·0685 gram Na_2SO_4, corresponding to ·0222 gram Na = 14·16 per cent. Na; theory, $C_7H_7NaO_3$ requires 14·19 per cent. Na.

Ethyl Pyrotritartrate, $C_7H_7(C_2H_5)O_3$.—On adding ethyl iodide to dry silver pyrotritartrate, reaction took place in the cold, so much heat being developed that the ethyl iodide was caused to boil violently. The reaction was completed by heating in the water-bath for an hour. The ethyl pyrotritartrate was extracted from the silver iodide formed by means of ether, and on distilling off the ether, a slightly yellow-coloured oil was left which had the same anise-like smell as the original oil from which the acid was obtained by saponification with soda. On distillation it boiled at 205—208°, but a small quantity of crystals of pyrotritartaric acid separated (melting point 135—136°), the formation of which was probably due to a trace of water remaining in the silver salt employed. To remove the acid the substance was mixed with a little ether and shaken with dilute potash, the ethereal layer dried with potassium carbonate, the ether distilled off, and the residual oil fractionated; the boiling point was again 205—208°, and now no crystals separated, and it was perfectly neutral to

test-paper. Owing to the small quantity of substance operated on, the boiling point appears a little lower than that of the original oil (208—209°).

·1889 gram gave on combustion ·4429 gram CO_2, and ·1265 gram OH_2.

		Theory $C_7H_7(C_2H_5)O_3$.	Found.
C	=	64·28	63·94
H	=	7·14	7·44
O	=	28·58	—

Böttinger (*Ann. Chem. Pharm.*, clxxii, 245) did not succeed in preparing the ether of uvic acid. He, however, found that reaction takes place between silver uvate and ethyl iodide in the cold, but he used ethyl iodide diluted with alcohol, which alcohol probably contained enough water to re-produce uvic acid. That a trace of water would have this effect during the formation of the ether is shown above.

Carbopyrotritartaric Acid.

The white crystalline substance, not volatile in steam, from the action of dilute sulphuric acid on ethyl diacetosuccinate, was recrystallised first from the mother-liquors containing sulphuric acid and then several times from boiling water. Dried at 100° and analysed it gave the following results:—

I. ·1549 gram gave ·2950 gram CO_2, and ·0723 gram OH_2.
II. ·1328 gram gave ·2539 gram CO_2, and ·0526 gram OH_2.

		Theory $C_8H_8O_8$.	I.	II.
C	=	52·17	51·93	52·14
H	=	4·34	4·46	4·39
O	=	43·49	—	—

In another preparation the residue, after distillation of the oil above described (ethyl pyrotritartrate), was not recrystallised from the mother-liquor, but at once from water. It was here noticed that the more difficultly soluble portions had a much lower melting point than the others, and fused to an oil before dissolving, so that the body appeared to be a mixture. An attempt was therefore made to separate the constituents by fractional decomposition of the sodium salts by means of dilute sulphuric acid. The sodium salt was prepared by neutralising with sodium carbonate. The first portions precipitated by sulphuric acid, when recrystallised from water, consisted of flat needles having a satiny lustre; they melted at 81—82°, and were capable of neutralising a solution of sodium carbonate when warmed with it. On analysis the following results were obtained:—

I. ·096 gram gave ·1943 gram CO_2, and ·0484 gram OH_2.
II. ·1104 gram gave ·2231 gram CO_2, and ·056 gram OH_2.

		Theory $C_8H_7(C_2H_5)O_5$.	Theory $2(C_8H_7(C_2H_5)O_5).C_8H_8O_5$.	I.	II.
C	=	56·60	55·26	55·21	55·11
H	=	5·66	5·26	5·60	5·63
O	=	37·74	39·48	—	—

On boiling this substance for some time with dilute sulphuric acid long slender needles were obtained on cooling, which when recrystallised from water melted at 230—231°. The latter precipitated fractions of the acid, also melted at 230—231° when treated in the same manner. The numbers obtained on analysis are—

I. ·1611 gram acid gave ·3045 gram CO_2, and ·0675 gram OH_2.
II. ·182 gram acid gave ·3435 gram CO_2, and ·0714 gram OH_2.

		Theory $C_8H_8O_5$.	I.	II.
C	=	52·17	51·55	51·47
H	=	4·34	4·66	4·36
O	=	43·49	—	—

The acid crystallises from boiling water, in which it is pretty soluble, in very fine long needles, especially if a little sulphuric acid be present. It is nearly insoluble in cold water. The sodium and ammonium salts have a persistent bitter taste, and both are easily soluble in water, crystallising out in long needles. The sodium salt is but slightly soluble in alcohol.

Analysis of Sodium Salt.

I. Specimen prepared from pure acid by neutralisation with sodium carbonate. ·2107 gram dried at 100° lost ·0409 gram = 19·41 per cent. OH_2. ·1698 dried at 100° gave ·0592 gram Na_2SO_4 = ·0191 gram Na = 11·25 per cent. Na.

II. Crystallised out of mixture of sodium salts prepared in order to make the fractional precipitation mentioned above. ·181 gram dried at 100° lost ·335 gram = 19·33 per cent. OH_2. ·1460 dry salt gave ·0515 gram Na_2SO_4 = ·01668 gram Na = 11·42 per cent. Na.

Theory—$C_8H_7NaO_5$ requires 11·16 per cent. Na.

„ $C_8H_7NaO_5 + 2\frac{3}{4}Aq$ requires 19·37 OH_2; $C_8H_7NaO_5 + 3Aq$ requires 20·77 per cent. OH_2.

Silver carbopyrotritartrate is thrown down from a solution of the sodium salt as a curdy precipitate, which is insoluble in cold, but soluble in much hot water with but slight decomposition, crystallising out in fine needles on cooling. It becomes grey on exposure to light,

but is a tolerably stable salt. On combustion the following numbers were obtained:—

I. ·1842 gram salt gave ·2217 gram CO_2, ·0421 gram OH_2, and ·067 gram Ag.

II. ·1229 gram salt gave ·1473 gram CO_2, ·0278 gram OH_2, and ·0448 gram Ag.

III. ·1632 gram salt gave ·0603 gram Ag.

		Theory $C_8H_7AgO_5$.	I.	II.	III.
C	=	32·99	32·82	32·68	—
H	=	2·40	2·54	2·51	—
Ag	=	37·11	36·37	36·44	36·94
O	=	27·50	—	—	—

There was a well-crystallised sublimate on the sides of the crucible, which melted at 230°, and was therefore carbopyrotritaric acid; the sublimate on the lid melted much lower (130°), and was probably pyrotritartaric acid formed by the decomposition of carbopyrotritartaric acid by heat.

Ethyl carbopyrotritartrate.—Silver carbopyrotritartrate was sealed up in combustion tubes with excess of ethyl iodide and heated in the water-bath for three hours. The contents of the tube were treated with ether, and the extracts on evaporation left the carbopyrotritartaric ether in the crystalline state and slightly brown-coloured. By recrystallisation from ether it was obtained perfectly white. It is soluble in ether, benzene, and alcohol, and when pure melts at 80—81°; it crystallises in needles, and when heated sublimes with partial decomposition. A combustion gave the following results:—

·09 gram substance gave ·188 gram CO_2 and ·0464 gram OH_2.

		Theory $C_8H_7(C_2H_5)O_5$.	Found.
C	=	56·60	56·97
H	=	5·66	5·73
O	=	37·74	—

In order to see if the original acid would be reproduced on saponification, the ether was boiled with dilute soda; on precipitation of the acid with sulphuric acid the melting point was 217°, but on further boiling with dilute sulphuric acid the melting point was 230°, showing it to be carbopyrotritartaric acid. It crystallises out in the characteristic long fine needles of the acid; the substance therefore is a true ethyl salt, the ethyl-group not being directly combined with carbon.

Behaviour of Carbopyrotritartaric Acid when Heated.—A small quantity was heated carefully in a test-tube with about double its weight of powdered glass; a sublimate was formed which was crystallised from ether and re-sublimed. It melted at 135—136°.

The experiment was repeated with a gram of acid and the gas evolved passed through baryta-water, in which a precipitation of barium carbonate took place. A small quantity of carbonaceous matter remained mixed with the glass. The glass tube containing the sublimate was cut off, the latter dissolved out with ether, the ether evaporated, and the residue re-sublimed. The melting point was 135—136°, and the following numbers were obtained on combustion:—

·1608 gram acid gave ·3546 gram CO_2 and ·0818 gram OH_2.

		Theory $C_7H_8O_3$.	Found.
C	=	60·00	60·14
H	=	5·71	5·65
O	=	34·29	—

So that the reaction taking place on heating carbopyrotitartaric acid is $C_8H_8O_5 = C_7H_8O_3 + CO_2$.

From the fact that carbopyrotritartaric acid splits up on heating into pyrotritartaric acid, which undoubtedly contains a carboxyl group and carbon dioxide, it appeared probable that it belonged to the class of etheric anhydrides, and that it would furnish a dimetallic salt when submitted to the action of alkalis.

In order to test this, ·6555 gram carbopyrotartaric acid was boiled for an hour with 7·5 c.c. of normal soda (·4 c.c. excess of the quantity required to form the dimetallic salt), but on titrating back with normal hydrochloric acid, 3·75 c.c. were added before the solution became neutral to litmus, so that the carbopyrotartaric acid had apparently used up only 3·75 c.c. sodium hydride solution; the monometallic salt would require 3·56 c.c., the dimetallic salt 7·12 c.c. It was, however, possible that the dimetallic salt might have an alkaline reaction.

Experiment 2. ·6704 gram acid was therefore treated with 1·94 c.c. of a soda-solution containing ·08625 gram Na per c.c., equal to ·1673 Na (the calculated amount to form this dimetallic salt is ·1676 gram). After a quarter of an hour the solution had still an alkaline reaction, and a small quantity gave with silver nitrate a brown precipitate containing silver oxide. The rest of the solution was heated for a short time, and after cooling silver nitrate was added to it, whereby a perfectly white precipitate was produced, showing that no free sodium hydroxide existed in solution, although the liquid still had an alkaline reaction. The silver precipitate was filtered off, washed, dried in a vacuum, and analysed, with the following results:—

I. ·2416 gram salt gave ·2143 gram CO_2, ·034 gram OH_2, and ·1279 gram Ag.

II. ·2144 gram salt gave ·1924 gram CO_2, ·0318 gram OH_2, and ·1135 gram Ag.

III. ·2602 gram salt heated carefully in a porcelain crucible left ·138 gram Ag.

		Calculated $C_8H_8Ag_2O_6$.	Found. I.	Found. I.	Found. III.
C	=	23·08	24·19	24·47	—
H	=	1·92	1·56	1·64	—
Ag	=	51·92	52·93	52·94	53·04
O	=	23·08	—	—	—

The analytical numbers would agree somewhat better with the formula $C_{16}H_{14}Ag_4O_{11} = 2C_8H_8Ag_2O_6 - H_2O$, which requires:—

C_{16}	=	23·59
H_{14}	=	1·72
Ag_4	=	53·07
O_{11}	=	21·62

The acid reprecipitated from this salt by dilute nitric acid was unaltered carbopyrotritartaric acid (m. p. 230°).

Carbopyrotritartaric acid boiled for some hours with strong potash was not decomposed, the reprecipitated acid melting at 230°.

Carbopyrotritartaric Acid fused with Potassium Hydroxide.—1·75 grams acid were fused with about 5 grams of potassium hydroxide until a small portion treated with sulphuric acid no longer gave a precipitate. The slightly brown fused mass was acidified with sulphuric acid and distilled. The distillate had a strong acid reaction, and smelt like acetic acid. A small portion, treated with H_2SO_4 and a drop of alcohol, gave the characteristic pleasant odour of ethyl acetate. The distillate was neutralised with sodium carbonate and evaporated to dryness, the residue exhausted with alcohol, and the alcohol driven off on the water bath. The white salt left was dissolved in water and precipitated with silver nitrate. The precipitate, on recrystallisation from a little hot water, gave the flat silky needles of silver acetate.

0·0738 gram left on heating 0·0476 gram, or 64·50 per cent. Ag. $C_2H_3AgO_2$ requires 64·67 per cent.

The residual liquid from which the acetic acid had been distilled was extracted several times with ether, which on distillation left a slightly yellow-coloured crystalline acid. It was dissolved in a little water, treated with animal charcoal, and the filtered liquid evaporated to the crystallising point; after recrystallisation from ether it was perfectly white, and melted at 180°. A small quantity on heating gave very irritating vapours, and a pale, red-brown precipitate was produced in a solution of the neutral ammonium salt by ferric chloride; a white insoluble precipitate was obtained with plumbic acetate.

This crystalline acid was, therefore, succinic acid, and the reaction taking place on fusion of carbonic acid with potash may be represented by the equation :—

$$C_5H_8O_5 + 3OH_2 = C_4H_6O_4 + 2C_2H_4O_2.$$

The foregoing observations show that on boiling ethyl diacetosuccinate with dilute sulphuric acid, two reactions take place simultaneously. On the one hand, the elements of ethyl alcohol are split off, ethyl carbopyrotritartrate being formed :—

$$C_{12}H_{18}O_6 = C_2H_6O + C_{10}H_{12}O_5;$$

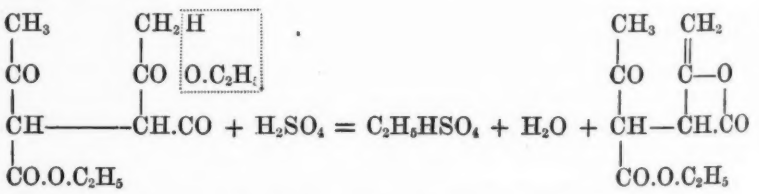
The latter is, however, soon resolved by the action of water into a second molecule of alcohol and carbopyrotritartaric acid,—

$$C_{10}H_{12}O_5 + H_2O = C_2H_6O + C_8H_8O_5.$$

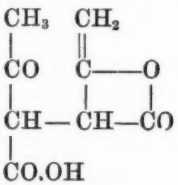
On the other hand, carbon dioxide and alcohol are both split off, pyrotritartaric acid being formed :—

$$C_{12}H_{18}O_6 + OH_2 = CO_2 + 2C_2H_6O + C_7H_8O_3,$$

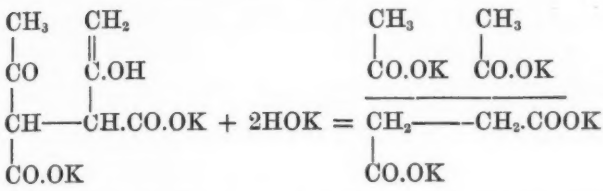
The fact that carbopyrotritartaric acid is at the same time monobasic acid and etheric anhydride, that by heating it is resolved into pyrotritartaric acid and carbon dioxide, and that it gives acetic and succinic acids on fusion with potash,—together with the known composition of ethyl diacetosuccinate,—furnishes the key to the composition of the two acids obtained from the latter substance. Thus the formation of ethyl carbopyrotritartrate probably takes place in the following manner :—



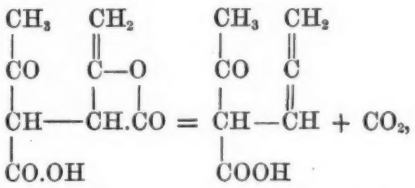
So that the formula of carbopyrotritartaric acid would be—



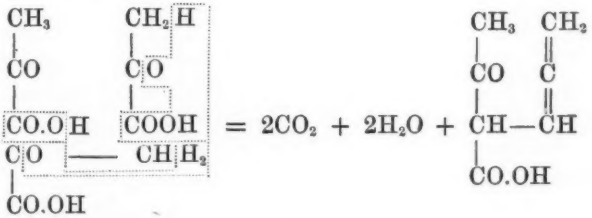
The production of succinic and acetic acids from the dimetallic salt formed by the action of alkalis may be represented by the equation :—



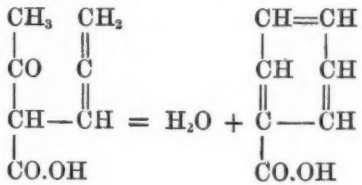
Carbopyrotritartaric acid when heated gives off carbon dioxide, forming the monobasic pyrotritartaric acid, thus:—



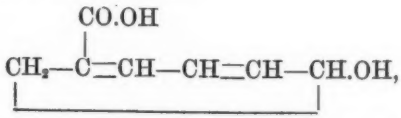
the production of which from pyruvic acid may be represented in the following manner:—



The formation of benzoic acid, which Böttinger got by adding uvic acid to fused potash, precipitating with acid, and resubliming, would be comprehensible from the above formula, although rearrangement of the hydrogen atoms would certainly have to take place:—



Böttinger's uvic acid formula—



would not explain the formation of the acid from ethyl diacetosuccinate,

and again, it cannot be the correct one, as Wislicenus and Stadnicki have proved that the acid does not contain a second hydroxyl group.

I have to thank Professor Wislicenus for the very kind help which he has given me in carrying out this investigation.

The research was conducted with a grant of 10*l.* obtained from the Chemical Society's Research Fund in July, 1877.

LIII.—*A New Test for Glycerin.*

By A. Senier, M.D., and A. J. G. Lowe, Assistants in the Laboratories of the Pharmaceutical Society.

In a previous paper (*Pharm. Journ.*, viii, 819), we have shown that when certain acid borates, as, for example, ordinary sodium biborate, are dissolved by glycerin, the glycerin does not act simply as a solvent. We found that acid was evolved, which was probably free boracic acid, and that there remained behind more basic borates, having a constitution between mono- and bi-borates. Klein (*Compt. rend.*, lxxxvi, 826) says that with acid borates mannite forms conjugated acids. He describes briefly some compounds obtained, and then says that similar reactions take place in the case of glycerin, erythrite, and certain other polyatomic alcohols. It is true that mannite, erythrite, &c., evolve acid with sodium biborate in the same manner as glycerin, but the reactions are probably not the same. The test which we are about to describe is not given by mannite, glucose, &c., although it is readily obtained from glycerin, erythrite, and apparently from glycol. We are at present investigating this reaction more fully. It is interesting, however, to note here, that while we find the action of glycerin and erythrite to differ from the action of mannite and glucose, Klein also finds the action upon polarized light different in the case of the two former, from what it is in that of the latter. The well known green colour which free boracic acid imparts to flame is usually obtained in the case of borates by the use of a stronger acid, but Iles (*Chem. News*, xxxv, 204) suggests that glycerin may advantageously be substituted for the acid. This glycerin test for boracic acid involves, of course, the reaction which we have just discussed.

It occurred to us that this reaction might also be employed as a test for glycerin, but before we describe the method of applying it to that

end, it will be convenient to discuss briefly its limits as regards other bodies. As might be anticipated from what we have said, monoborates do not give this reaction, at least that is the case with sodium monoborate. A considerable quantity of alkali interferes with the test, doubtless by neutralising and fixing the acid set free. Again, a large excess of borax itself prevents the appearance of the green colour in the flame. This action of a large excess of borax is interesting. Now as to bodies which may be mistaken for glycerin. Acids give the same result to flame as glycerin, and hence the solution to be tested must be neutral or faintly alkaline. Erythrite, and apparently glycol, also give the same green flame, but could hardly occur so as to be mistaken for glycerin. The same may be said of copper salts and certain other substances, which of themselves might impart a green colour to flame. Other substances, such as sugars, fats, &c., were tried, but all failed to give this test. It appears, then, in the absence of erythrite, and probably glycol, to be a property fairly characteristic of glycerin.

The test is applied as follows:—The aqueous solution to be examined is first made slightly alkaline with dilute soda-solution, and a borax bead is dipped into it. The bead is allowed to rest for a minute or so to allow solution to take place on its surface. Then it is held in the Bunsen flame in the usual way. Another method, and this we find more delicate, is to place a little powdered borax on a watch glass, and pour on to it some of the solution made faintly alkaline. Stir with a glass rod (the mixture becomes acid of course), and by means of a looped platinum wire introduce some of the mixture into the flame. In either case the deep green colour appears more or less distinctly if glycerin be present in sufficient quantity.

The following experiments were made with the view of determining the extent to which the test could be applied to the detection of glycerin in various solutions. The percentages are by volume.

Glycerin in Water.—The solutions were made faintly alkaline. A 20 per cent. solution gave the colour very decidedly. Solutions containing 15, 10, and 5 percentages gave the colour distinctly. 2½ per cent. gave a faint colour, and the limit seemed to be reached in the case of a 1 per cent. solution, which gave scarcely any colour.

Glycerin in Beer.—The solutions were made faintly alkaline. 25 and 20 per cent. solutions gave the colour decidedly. A 10 per. cent. solution gave it distinctly, but in the case of a 5 per cent. solution it could scarcely be seen. It was evident from these experiments that, in order to detect less than 10 per cent. in beer, the solution of glycerin would have to be concentrated, and some of the foreign matter removed. To try this we prepared two solutions of glycerin, one containing 5 per cent. and the other 1 per cent. Both were treated in the same manner. 50 c.c. were evaporated to dryness over a water-bath,

and the residue was treated with 50 c.c. of absolute alcohol. Solution of the glycerin in the alcohol was insured by well stirring the mixture and heating to boiling. The dish containing the mixture was then set aside to cool and subside, after which the clear alcoholic solution containing the glycerin was decanted into another dish. The solution was evaporated to dryness as before, and again exhausted with absolute alcohol. The solution from this second treatment with alcohol was evaporated nearly to dryness, and a few drops of water added. The solution thus obtained was made faintly alkaline to delicate litmus paper with dilute soda solution, and tested in the manner already described. In each case the colour was distinct, of course most decided in the case of the residue from the 5 per cent. solution. A solution containing one quarter of 1 per cent. was examined in the same way, and gave the colour distinctly. Beer, to which was added only one-tenth of 1 per cent. of glycerin was examined by first concentrating and shaking with petroleum ether, to remove hop resin, and then evaporating to dryness and treating as above. In this case the green colour, though less intense than before, was distinctly seen. Several experiments were made with beers to which glycerin was not added; but treating them in the way described no green colour could be obtained. It was noticed that the consistence of the residues from beers to which glycerin had been added, compared with the residues of beers containing no glycerin, was very different. The former were, of course, moist and syrupy, while the latter were much harder and even brittle.

Glycerin in Wine.—To some sherry wine was added 1 per cent. of glycerin. Of this solution 50 c.c. were evaporated to dryness over a water-bath. The residue was treated, as previously described, with 25 c.c. of absolute alcohol. The alcoholic solution was then evaporated over a water-bath nearly to dryness, and a few drops of water added. This solution, made faintly alkaline and tested, gave the green flame distinctly. The same wine without glycerin gave no green colour to flame.

Glycerin in Milk.—100 c.c. of milk, to which 1 per cent. of glycerin was added, were evaporated to dryness over a water-bath. The residue was treated with 50 c.c. absolute alcohol, and the alcoholic solution so obtained evaporated to dryness as before. A few drops of water were added, and the mixture filtered through a moistened filter to separate fat. The filtrate was then rendered alkaline and tested. The green colour was distinctly observed. 100 c.c. of milk without glycerin similarly treated gave no green colour. The fat of milk likewise gave no colour reaction.

Glycerin in Treacle.—50 c.c. of treacle, in which was dissolved by aid of heat and agitation 5 per cent. of glycerin, were, while warm, well

agitated with absolute alcohol. The mixture was set aside, and allowed to cool and separate. The alcoholic solution was then decanted, and evaporated over a water-bath to dryness. This residue was treated with 50 c.c. of absolute alcohol in the usual way, and the alcoholic solution so obtained evaporated over a water-bath to dryness. This second residue was treated in the same way with 25 c.c. of absolute alcohol, and the solution obtained was evaporated as before. The residue was diluted with a few drops of water, and the solution made faintly alkaline. Tested, it gave the green colour distinctly. A 1 per cent. solution failed to give the reaction, thus showing at the same time that treacle itself treated in this way is incapable of producing the green colour.

It may be said then of the test for glycerin here proposed that it is practically characteristic, and is delicate. It can be easily applied, and is not interfered with by the presence of a considerable quantity of foreign matter. We therefore commend it to trial by chemists as a substitute for the known tests for glycerin, which are not only few but objectionable.

In conclusion we have to express our indebtedness to Mr. H. G. Greenish for valuable assistance, and to Professor Attfield for kindly permitting these experiments to be conducted in the Laboratories of the Pharmaceutical Society.

Authors' Note.—In the discussion which followed the reading of the above paper our attention was directed to the fact investigated by Woodcock (*Jour. Chem. Soc.*, xxiv, 785), that ammoniacal salts have the power of decomposing borax and liberating boracic acid. It was suggested that these salts might be mistaken for glycerin unless further precautions were taken. We find this to be the case.

Substances to be examined for glycerin by the test we have suggested should be first tested for ammonia, and should this be present the above methods must be so modified as to secure its complete exclusion. To determine the presence of ammonium salts, sodium carbonate, and in some cases the Nessler reagent, should be employed. The following two experiments will suggest how ammonium salts may be separated. When fats occur they must, of course, be removed prior to treatment with alkali.

50 c.c. of an aqueous solution, containing 1 per cent. each of ammonium chloride and glycerin, were evaporated in a platinum dish over a water-bath to dryness. Saturated solution of sodium carbonate was then added, and the heat of the water-bath continued until no more ammoniacal gas was evolved, and the mixture was distinctly alkaline. The mixture was then extracted with absolute alcohol, and the

solution evaporated, neutralised, and tested. The green colour was distinctly seen.

50 c.c. of beer, containing 1 per cent. each of ammonium chloride and glycerin, were evaporated to dryness over a water-bath. The ammoniacal salt was separated from the residue as before. The mixture thus obtained was treated with absolute alcohol, as described in the paper, and tested, the final solution being neutral, or only faintly alkaline. The green flame was very distinct. 50 c.c. of beer containing ammonium chloride only were examined in the same way, but gave no green colour to flame.

LIV.—*On the Preparation of Metallic Chlorides.*

By Charles W. Watts, and Chichester A. Bell, B.A., M.B., of University College, London.

The two principal processes for the preparation of chlorides in the dry way consist in (1), passing chlorine over the heated metal; and (2), passing chlorine over a mixture of the oxide with charcoal. The first is usually troublesome, on account of the difficulty attending the preparation of many of the metals; and the second, on account of the fine state of division to which it is necessary to reduce the oxide, if it is desired to obtain any considerable portion of the metal in the state of chloride. This being the case, it appeared advisable to find some more convenient process, and carbon tetrachloride seemed likely to afford a means for the preparation of metallic chlorides, and more especially of the higher chlorides.

The first experiment tried was with stannic oxide. The anhydrous oxide was placed in a long porcelain tube, connected at one end with a small retort, in which the carbon tetrachloride was kept in a state of gentle ebullition, and at the other with a cooled receiver. When the tube was heated to bright redness, and the vapour of carbon tetrachloride passed slowly over the oxide of tin, a liquid soon began to collect in the receiver, accompanied by a small quantity of a yellowish solid, either oxychloride or hydrated chloride of tin. Carbonic acid and chlorine escaped from the receiver (the chlorine being derived from the decomposition of some of the carbon tetrachloride), and a small quantity of stannous chloride was deposited in the cooler parts of the tube.

When the contents of the receiver were fractionally distilled, a small

portion came over at about 80°, consisting for the most part of carbon tetrachloride, and the principal portion of the liquid distilled over at 118—120°, the boiling-point of stannic chloride; it fumed strongly in the air, and united violently with water, forming a solution of stannic chloride. The product amounted to about 40 per cent. of the tetrachloride used. A small quantity of solid product was left in the distillation flask, subliming in white needles, and consisting of carbon monochloride, C_2Cl_2.

The next oxide used was titanic acid, the experiment being conducted in precisely the same way as with stannic oxide. The titanic acid was introduced into the tube in lumps, about the size of buck-shot. The product amounted to about 50 per cent. of the tetrachloride used; it was accompanied by a small quantity of ferric chloride. The residue in the tube consisted of unaltered titanic acid, and of skeletons of the lumps of titanic acid, consisting probably of silica. Similar experiments were tried with silica, both precipitated (from SiF_4) and well-burnt black flint. The tube, about 30 inches long, was heated nearly to whiteness, but in both cases only the merest traces of silicon chloride were obtained, even with the most efficient condensing arrangement.

Tungstic acid and carbon tetrachloride gave a mixture of WCl_4O, and WCl_2O_2, the principal reaction being probably expressed by the equation—

$$WO_3 + 2CCl_4 = 2WO_2Cl_2 + WOCl_4 + 2CO_2.$$

A similar experiment with chloroform and titanic acid gave a quantity of titanic chloride, equal to about 30 per cent. of the chloroform used. A large quantity of secondary product was obtained, consisting of titanium oxychloride, chlorides of carbon, &c.; a notable proportion of the titanic chloride was also carried off by the gases, hydrochloric and carbonic acids, produced in the reaction. The formation of titanous chloride was not noticed.

Carbon tetrachloride being somewhat expensive, and a notable proportion being always lost, a mixture, in equal volumes, of carbonic oxide and chlorine was tried as a means of producing these chlorides. With titanic acid a very good result was obtained, although some quantity of the titanic chloride was carried off by the carbonic acid produced, which has double the volume produced with carbon tetrachloride: $TiO_2 + 2CO + 2Cl_2 = TiCl_4 + 2CO_2$. Silica again was hardly acted on. Tungstic acid gave a mixture of the two oxychlorides, but when a larger proportion of carbonic oxide was used, a small quantity of nearly black crystalline chloride (WCl_6 or WCl_5) was obtained. 5 grams of tungstic acid placed in a small porcelain tube and heated to full redness, was entirely volatilised as oxychloride after

about 3 litres of gas had been passed over it. Amorphous chromic oxide was acted on with great readiness, the crystalline oxide not quite so easily; in both cases, however, an abundant production of chromic chloride resulted, which, when the tube was heated a few inches beyond the oxide, was non-deliquescent, and completely insoluble in water, showing the absence of any chromous chloride.

Red oxide of manganese, Mn_3O_4, free from iron, was acted on very easily, but the chloride being non-volatile, it could not be perfectly separated from the unaltered oxide. A very small quantity of apparently colourless crystals, containing manganese and chlorine, sublimed to the mouth of the tube at the beginning of the experiment, but the amount was too small for further examination.

A similar experiment was tried with bromine, carbonic oxide, and stannic oxide. The dry carbonic oxide was bubbled through bromine kept warm in a small retort, and covered with strong sulphuric acid to prevent surface evaporation. Stannic bromide volatilised into the receiver, and some stannous bromide was left in the tube.

In all these experiments the carbonic oxide was previously prepared, and stored in a gasometer. Experiments were made in which a mixture of 1 vol. carbonic acid with 2 vols. chlorine, was passed through a tube, three parts filled with carbon, and the rest with oxide, separated from one another by a plug of asbestos. Both wood-charcoal and coke were found very wasteful of chlorine, on account of the hydrogen they contain; and with gas-carbon, although carbonic acid alone was easily converted into carbonic oxide, the mixture of chlorine and carbonic acid passed through almost unchanged.

These experiments were made in the Laboratory of University College. The authors intend pursuing the subject, more especially with regard to the higher chlorides.

LV.—*Laboratory Experiences on board the "Challenger."*

By J. Y. Buchanan.

[A Lecture delivered before the Chemical Society, February 21st, 1878.]

In commencing my lecture upon laboratory experiences on board the "Challenger," it will be fitting that I should describe the laboratory in which they were made.

The laboratory was situated on the main deck, just abreast of the mainmast, and therefore almost exactly in the middle of the length of the ship, on the right-hand side looking forward. It was lighted and ventilated by a port, which under ordinary circumstances would accommodate a gun. Besides this window or port there were windows into the deck, capable of supplying a certain amount of borrowed light. Against the foremost partition was fitted a locker, the top of which formed a seat, and indeed occasionally a bed, and the interior formed a storehouse for instruments and spare apparatus. Above it, and fixed to the same partition, were two book-shelves, which accommodated the greater part of our chemical literature. In front of the seat was a writing-table, attached at one end by hooks to the one sash of the window, and supported on the other end by folding iron legs. It was capable of easy removal, and indeed was only "shipped" when the laboratory became a study. On the other side, in front of the seat, was a blow-pipe table, of common deal, with a double action circular bellows, of eight inches diameter, underneath.

A tallow lamp was supplied to me for use with the blowpipe, as being the kind of lamp used by glass-blowers by trade. No doubt, for such persons, it is suitable enough, but in a laboratory a blowpipe is wanted often for a few minutes at odd times, when it would be impossible to spend the time necessary for the preliminary melting of the tallow, and I finally adopted a spirit-lamp, made out of a wide-mouthed four-ounce bottle, with a piece of metal made to take a wick just as broad as the mouth would accommodate, and with it it was possible to do every sort of glass blowing that was necessary. The blowing of lead glass was especially easy with it. The wind from the bellows was directed across the burning wick by means of a glass jet in the ordinary way. For delicate glass blowing an arrangement of this sort is preferable to any of the forms of gas blowpipe, because there is not the glare of the smoky flame, and moreover lead glass can be worked with

the utmost facility without blackening, and those who have conquered their first repugnance to lead glass, and have learned to work it, know how much pleasanter it is to handle than even the softest German glass.

On the sternward side of the window was the working bench, which was constructed of teak. The height was 3 feet 10 inches, which was found extremely convenient for working at, as there was no necessity for bending. It was fitted in the usual way with drawers. The reagents also were accommodated in drawers. Each bottle was partitioned off, so that in the rolling of the ship they could not roll against each other. For smaller bottles these drawers were divided in the middle, so as to form two trays, one behind the other. This arrangement was convenient, because a drawer filled with reagent bottles could thus be taken out and put upon the bench for use. It was not liable to be disturbed by the rolling, because it was kept in its place by the battens which surrounded the table. In order to support flasks or apparatus of any kind, it was of course impossible to take the ordinary retort stand of the laboratory, because it would be difficult to fix it in such a way as would not be absolutely permanent and still secure. I therefore adopted this stand, taking the metal rod, half an inch in diameter, which is used for retort stands, having a longitudinal eye forged upon it like the eye of a needle, which was then fastened into the beam here by an eye-bolt, and had therefore a certain amount of play up and down. The rod was then shoved into a hole in the thick teak board on the top of the working bench, the retort stand rings and lamp, such as a spirit-lamp, being slipped up from below before having the rod put into the hole in the top of the bench. This was an exceedingly convenient apparatus, because when not in use it could be slipped up, and the rings taken off from below, and the rod put up against the roof with its end in a hook overhead, and therefore out of the way. This was used then for setting up apparatus such as that for determining the carbonic acid, to which I shall refer presently. For drying and evaporating, a cast-iron gimbal support was fixed to the ship's side. It was capable of carrying a sand-bath or water-bath, or drying chamber, always in a level position.

In the corner there was a sink, that is to say a pipe, which led away to a scupper, draining water off the main deck. Distilled water, supplied by the boiler of the ship, was kept in a bottle, and always ready for supply.

The glass apparatus was arranged in the ordinary way, on shelves with double perforation to keep each article in its place. Up above, the beams which support the deck were of considerable dimensions. They projected about 9 inches down from the deck above, so as to afford considerable room between them. These were all taken

advantage of for putting away apparatus and articles which were not in constant use.

The burettes were fixed to the shelves. They resembled graduated pipettes, the lower end being fitted with a pinchcock. To the upper one an india-rubber tube could be fixed with a glass tube for sucking. When any reagent was going to be used in the burettes, a glass tube of such length as to reach well down into the bottom of the bottle was attached to the point of the burette, and plunged into the liquid, which was sucked up into the burette.

One of the reagents in constant use was baryta-water for the determination of the carbonic acid in the sea-water. By using this method of filling the burette, so that none was spilt on the neck of the bottle, no more liquid was used than was absolutely necessary, and no more air got into the bottle than there was liquid taken out of it. A bottle holding rather more than a litre would last two or three months; and, taking a portion each day, its standard did not alter sensibly.

The remaining arrangements are not of any special interest, and need not therefore be further referred to.

The principal defect of the laboratory was the want of means of removing noxious vapours. From the position in the ship it was found impossible to provide any kind of draught chamber, the only means of ventilation being by the door or window; hence mineral analysis of any extent was rendered impossible.

The dimensions of the laboratory were ten feet long and five feet eight inches wide, the height being exactly six feet at the highest part.

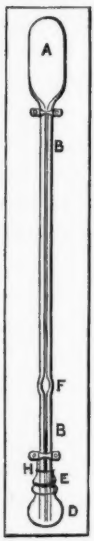
The space therefore was somewhat confined, but for one worker it was quite sufficient, and after getting accustomed to the motion of the ship, there was no great difficulty in working in all ordinary weather. In fact, as long as the weather was not so boisterous as to make it necessary to close the outside port, the work could always be done. With the port closed, light and ventilation were shut out and work became impossible on that account alone, even supposing the ship had been steady enough.

Having thus described the nature of the laboratory, I shall go on now to notice the experiments made with these instruments. Before starting on the expedition, it appeared to me to be of great importance to have some means of controlling the depth as ascertained by the sounding line. The records of deep sea soundings contained depths of as much as 8,000 fathoms, which had been obtained by various observers without bottom having been reached. This was explained by saying that in the ocean if there is no current at the surface, there is such a multitude of under-currents going in ways which cannot be seen or

estimated, that all sounding in this way must be fallacious. Of course having no practical experience of it myself, I could form no opinion, but I thought it was desirable to endeavour to have some means of checking the depths as given by the sounding line, and the first and most ready means which occurred to me was to adopt the barometric method. After studying and experimenting in various directions, I decided to adopt as a measure of the pressure the apparent contraction produced by it in a mass of water enclosed in a glass envelope.

During the spring of 1872, I made experiments on an instrument of special dimensions in the deepest water which was to be had near home, namely, in Loch Lomond, where the depth in some parts is as much as 105 fathoms. I thus found that the method was capable of practical application. In Fig. 1 the piezometer is depicted in section. It consists essentially of a thermometer-shaped instrument open at the end. A cylindrical bulb, A, contained, in the one that was chiefly used, about 9 c.c. The stem, which was rather more than a foot long, had a diameter of almost exactly one millimeter. The end of the stem dips into the bulb, D, which was filled so far with mercury, and the instrument was set by heating it to such a temperature, that when it cooled down to the atmospheric temperature the mercury would rise to a convenient height so as to be visible and to be able to be read at any moment at a given temperature by plunging it in water. The arrangement for protecting the open end of the instrument is somewhat peculiar. It is necessary to allow the water on the outside to get access to the mercury in the bulb in order that the pressure may exert itself, in the interior of the instrument, in the same way as air must have access to the mercury in the reservoir of the barometer. At the same time it is of importance that the mercury should not be able to come out of the bulb. The means, therefore, that have been taken for this purpose was to have a bulb, D, blown, into the neck of which the stem of the instrument fitted with some accuracy. This was connected with the stem by means of a piece of india-rubber, which was prevented from fastening hermetically on the stem by having a small piece of glass rod, H, shoved in between the india-rubber and the stem. In this way communication was constantly kept open between the outer water and the mercury in the bulb.

FIG. 1.



The stem of the instrument was divided into millimeters, and was carefully calibrated, the weight of the water filling the instrument, and also the coefficient of expansion of the glass were at the same time determined.

If the position of the water-mercury meniscus in the stem be noted under observed conditions of temperature and pressure, and the instrument be then observed under different conditions of temperature and pressure, the apparent volume occupied by the water, and therefore the position of the meniscus, will depend on the difference of the combined effects of temperature and pressure on the water and on the glass. This resultant effect is measured by the position of a magnetic index similar to or in fact exactly the same as that used in Six's thermometer. The deep-sea thermometer which was used was after Six's pattern, with a protected bulb. When the instrument is subjected to increased pressure or diminished temperature, or both together, the index is pushed up by the mercury, which enters owing to the decrease of temperature and the increase of pressure, and its position thus gives us the sum of the effects of change of pressure and of temperature on the apparent volume of the water.

If now, along with this instrument a sufficiently protected thermometer has been attached to the line, and its readings are taken at the same time, we have a measure of the temperature to which the instrument has been subjected. Knowing the dimensions of the instrument in every particular, and its behaviour under varying conditions of temperature, we can subtract from the whole reading of the instrument that which is due to temperature, and the remainder is that due to pressure. If we know the coefficient of apparent compressibility of the liquid, the depth is given at once.

Now before starting, I thought that the pressure would be more accurately measured by means of a gauge attached to a hydraulic pump, such as that used by Mr. Casella for testing the strength of the protected bulbs of the deep-sea thermometers. Mr. Casella was good enough to put his pump at my disposal for experiments on my original instruments, and their performances were satisfactory.

After we had been at sea for some time, and had made some experiments on the sounding line, it became evident from the readings that the depths so found were not to be relied upon—that in point of fact the gauge which had been used to determine the pressure was not a trustworthy standard, and on reflecting upon the matter, it became evident that in cases where one has a satisfactory sounding, there is no better gauge of pressure than the length of the sounding line. I consequently then directed my attention to determine the apparent compressibility of distilled water and some other liquids by means of the sounding line, that is to say, using the sounding line as the gauge of pressure, and taking particular care to observe that these experiments were made when the sounding was not vitiated by perturbing causes. When currents are present, they are always very evident from the behaviour of the sounding line. If the sounding line

remains vertical during the whole of the sounding, then we may be perfectly certain that there is no disturbance from currents either at the surface or below. If there is a current of any appreciable force, the sounding line begins to wander about, and has to be followed by the ship. This is an operation of considerable delicacy even in good weather, and in bad weather, when the winds and currents cross and complicate each other, it is one which calls for the highest skill on the part of the officer in charge. There is therefore no difficulty in determining if a sounding has been good, and only such soundings free from vitiation by any of the above-mentioned perturbing causes were used for our purpose.

It was only after we had been for a considerable time at sea—in fact, when we were really on the way home, that I was able to make a sufficient series of experiments with this instrument to determine satisfactorily the apparent compressibility of water. The instruments occasionally got out of order, and other work prevented my immediately putting them right. Then it was necessary to get a certain amount of skill in working, because repairing instruments of this kind especially at sea was not learnt in a day. The indexes worked very well in the deep-sea thermometer containing a solution of carbolic acid, which appears to preserve the elasticity of the hair (the spring of the index is a human hair, which clings to the side of the tube and keeps it in position), but not so well on being immersed in distilled water or saline solution, which seems to have the effect of impairing the elasticity in a certain length of time. The consequence was that the indexes began to get loose, and in the unavoidable jars of sounding they were shaken from the position which they had taken up at the deepest part, and became untrustworthy. And here is where the usefulness of the removable mercury bulb into which the stem dipped became apparent. Supposing the end had been permanently fitted with any of the glass blower devices, such as a double safety bulb, there would have been no means of getting at the inside of the instrument, which would thus have become useless as soon as the index had become loose. By the very simple operation of removing the instrument from the ebonite backing, slipping the bulb off and warming the instrument to expel the mercury from the stem, the index could be taken out with a magnet and a fresh hair put on and the instrument set again, when it was as good as new.

In this way, then, a number of experiments were made when the ship was on the way home between Tahiti and Valparaiso, in a long stretch of water of moderate depth, that is to say, between 2,000 and 2,500 fathoms, where the soundings were always very satisfactory; the weather was tolerably good, and there were no apparent currents at all. Fifteen very satisfactory soundings were thus obtained with

this instrument, and the result was to give the coefficient of mean apparent expansibility of distilled water in glass as 0·0009 per 100 fathoms of average sea-water. This corresponds to 0·0000491 per atmosphere, which is not very different from what Regnault obtained at very low pressures, and Aimé experimenting in the Mediterranean got 0·0000486 per atmosphere. I have used, however, as the unit always 100 fathoms, because for our purposes it is more convenient. From experiments made with another instrument at an earlier date, the mean apparent compressibility of water at pressures between 0 and 3,000 fathoms was found to be 0·000878 per 100 fathoms.

In an instrument precisely similar the compressibility of sea-water was determined. The results obtained were very concordant. Up to 800 fathoms the apparent compressibility was 0·000770, up to 1,000, 0·000787, and 1,500, 0·000793, the temperature being between 2° and 3° C. The mean value is 0·000783, and the ratio to the apparent compressibility of distilled water is 0·87. The dimensions of the instrument did not allow of its being used at greater depths.

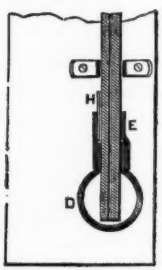
These experiments were all made on the sounding line, and at temperatures which were comparatively low. At all depths above 800 or 1,000 fathoms the temperature of the ocean varies but little. It is always somewhat under 4°, and generally under 3° C., and usually above 1° C., so that it may be said that these compressibilities are good for an interval of temperature between 1° and 3° C. In order to find out the compressibility at higher temperatures, there was on board a hydraulic instrument, similar to what Mr. Casella used for testing his thermometers. It was somewhat larger than Mr. Casella's, made for the purpose of being taken away. In it a number of experiments were made at different temperatures. But here we had no gauge, except an artificial one, which we found already was not to be relied on. Consequently the only determination that could be made was the relative apparent compressibility of various liquids, referred to that of distilled water as unity. Adopting one of the instruments filled with distilled water which had been used frequently on the sounding line as a gauge, we knew approximately what the pressure was, but we could not of course say that a compression of a certain amount at 20° C. represented the same pressure as the same compression at 2° C., and consequently in the result of these experiments I have only put down the *relative apparent compressibility* of these substances. The apparent compressibility of distilled water at the temperature of the water of the pump being unity, the relative apparent compressibility of sea-water and of a 4 per cent. chloride of sodium solution at different temperatures are given in the following table:—

Temperature C.	Relative apparent compressibility of			
	Sea-water.	4 p.c. NaCl solution.	Mercury.	Distilled water.
26·5°	0·9360	0·9051	—	1
25·8	0·9191	0·8813	—	1
22·5	0·9214	—	0·0301	1
22·1	0·9283	0·8661	—	1
13·7	0·9264	0·8684	0·0260	1
13·3	0·9203	—	0·0247	1
2·5	0·8950	—	0·0325	—

The relative apparent compressibilities appear to diminish with the temperature. This probably is owing to the fact that the compressibility of distilled water was found by Regnault, at low pressures at least, to diminish with the temperature. Now the compressibility of sea-water probably does not diminish so much, and that of chloride of sodium probably still less—possibly it even increases with the temperature. These results at any rate would tend to show that the compressibility differs in that direction. In the fourth column of the table the values of the relative apparent compressibility of mercury are given. To this I shall now refer. The compressibility of mercury was determined in an instrument (Fig. 2) the same as the water-piezometer; the stem,

FIG. 3.

FIG. 2.



however, was bent round, so that the mercury should not have a tendency to flow down the stem. The bulb, A, contained about 250 grams of mercury, about 19 c.c. The stem was filled with water through a

considerable portion of its length, BC, in which a magnetic index worked. This instrument was finished off in exactly the same way as the water-piezometer, that is, by dipping the open end into a cup of mercury (see Fig. 2). Here again the instrument registered the sum of the effects of temperature and pressure. On the sounding line experiments were made with this instrument. A number of observations were obtained at 800 fathoms and at 1,000 fathoms, with very concordant results. There were a number at other and greater depths, and those were plotted in the ordinary way on paper, and through them an average line was drawn, so as to give the compressibility of the mercury. The result was, that the apparent compressibility of mercury for 100 fathoms was 0·0000271, being per atmosphere 0·0000015.

Similar observations were then made in the pump. The results are given in the annexed table.

Temp.	Comp.
22·3	0·0301
13·3	0·0261
11·5	0·0247

There is a remarkable difference in the result at 11·5° and 13·3° from those obtained at lower temperatures than at 22·3° in the pump. The results at 11·5° and 13·3° C. were obtained by two different instruments, and are each the mean of about 15 different observations, so that they are probably correct. On the sounding line, at temperatures between 1° and 3° C., the relative apparent compressibility of mercury was found to be 0·0322, 0·0327, and 0·0301 in three different series of observations. It is impossible to say to what the low relative apparent compressibility at these temperatures is due, and the subject is worthy of further investigation.

Having then determined in this way the apparent compressibilities of these liquids, it was easy to apply it to the practical purposes of sounding. One of these instruments was attached to the line, and the apparent contraction cleared for temperature gave the depth.

It was, however, found that in many places the temperature remained apparently constant for a considerable depth; that is to say, after a certain depth, we will say, for instance, 1,000 fathoms, was reached, then if the depth of the sea was perhaps 2,500, the readings of the Casella thermometer showed constantly the same temperature all the way from 1,000 fathoms down to the bottom. This afforded evidence that either the temperature was the same all the way from 1,000 fathoms down to the bottom, or it was higher than at 1,000 fathoms; but there were no means of ascertaining this unless the temperature really rose to be higher than that at the surface, where of course the

maximum index of the Millar-Casella thermometer showed it. For this purpose the mercury-piezometer came into use, and it was for that purpose principally it was made. As in the case of the water-piezometer, its readings show the combined effect of change of temperature and of pressure, either of which being given the other can be deduced.

But it will be evident that if, after reaching a certain depth, the temperature remains constant, the apparent volume of the liquid will diminish in simple proportion to the increase of pressure, and if the temperature increases from a certain depth downwards, the apparent volume of the liquid will diminish in a less proportion than the increase of pressure. If this increase of temperature is such as to expand the liquid so as just to compensate the compressing influence of increase of pressure, the index will remain stationary. The method of using the two instruments combined will be evident from a reference to the figure.

The change of volume of water with change of temperature at the low temperatures found in the deep seas is very slight. The change of volume of mercury, however, for all ordinary temperatures is very considerable. On the other hand, the compressibility of water, or its sensibility to change of volume with change of pressure is very great, whereas that of mercury is very small. Consequently, by sending a pair of these instruments down upon the sounding-line, and reading them when they come up, we have two independent values of the sum of the effects of change of temperature and of pressure. Taking as the first approximation to the depth the length of the sounding-line, applying it to the reading of the mercury instrument, and so correcting it for pressure, we have a first approximation to the temperature; applying this temperature to the reading of the water-piezometer, we obtain a second approximation to the depth, indeed the true depth. The reading of the mercury-piezometer now being corrected for pressure by this value of the true depth, we have a second approximation to the temperature. In fact we have now practically the true depth and the true temperature. In the figures the thick lines represent the apparent changes of volume for change of pressure, and the dotted lines the apparent changes of volume for changes of temperature.

Fig. 4, *a* refers to the water-piezometer, and Fig. 4, *b* to the mercury-piezometer. Distances measured along the horizontal line of abscissæ represent depths in the scale of 0·01 inch to a fathom, and temperatures on the scale of 0·1 inch to a degree Centigrade. Distances measured along the line of ordinates represent scale divisions (millimeters) on the scale of 0·1 inch to a division. For 100 fathoms of depth the apparent contraction of the mercury instrument was 0·7 millimeter on the stem; in the water instrument the apparent contraction for 100 fathoms was somewhat over 7·8 millimeters. Considering that the effect of a change of temperature of 1° C. causes an

apparent change of volume represented by about 2·5 millimeters, while in the water-piezometer at the low temperature always found in deep

FIG. 4, *a*.

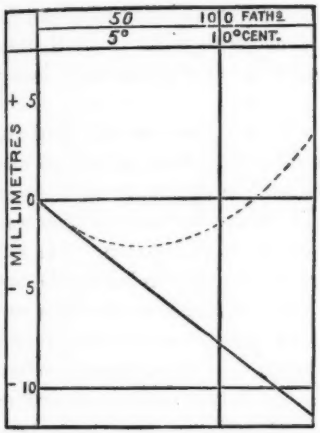
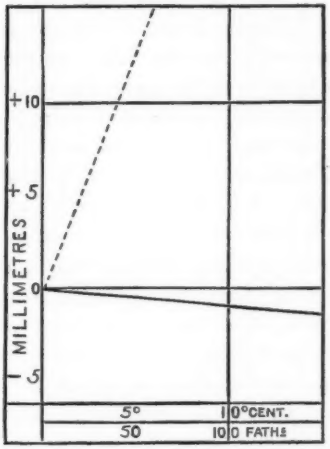


FIG. 4, *b*.



seas the temperature may be anything between 0° and 10° C. without altering the apparent volume of the water by more than 2 millimeters on the stem, we see that an error in determination of the depth of 100 fathoms would only make a difference in the reading of the mercury instrument of about 0·6 millimeter, equivalent to a difference of temperature of about 0·25° C. Therefore, applying the possibly erroneous depth given by the sounding-line to "clear" the reading of the mercury-piezometer for effect of pressure, we obtain a first approximation to the temperature which would almost always be within half a degree of the truth, but which might occasionally differ more than a degree from it. Using the temperature thus found to clear the reading of the water-piezometer for the effect of temperature, we obtain a second approximation to the depth which cannot differ appreciably from the true depth. Applying the depth so found to clear the reading of the mercury instrument for effect of pressure, we obtain a second approximation to the temperature which cannot differ appreciably from the truth. This process of gradual approximation may of course be carried as much further as we please, but the results obtained in the second approximation may under all circumstances be taken as representing the truth.

In Fig. 1 (page 448) the stem of the water-piezometer is represented as being swelled into a small bulb at F. The purpose of this bulb is to enable the instrument to be used at depths so great that with a uniform stem the contraction produced would be equal to the whole volume of the stem. The capacity of F is equal to the contractions

produced by the fall of temperature and the first 1,000 or 1,500 fathoms of depth, so that the instrument would only register depths greater than 1,000 or 1,500 fathoms, but it would do so with as much precision as can be obtained for less depths.

I also made an attempt to determine the compressibility of glass, in order to get the true compressibility of these liquids. I shall only allude to it in order to indicate the method—the result not being sufficiently accurate to be applied yet.

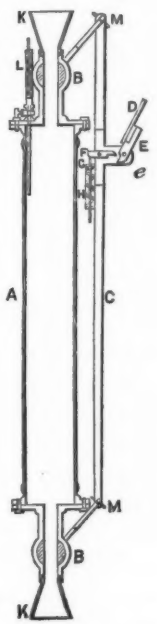
A tube such as that used for the stems of the piezometers, of about 1 millimeter bore, and graduated into millimeters, was sealed at one end. A glass rod was then drawn out to such a size as to pass easily into the tube, and about 2 inches shorter than the tube, which was made of the extreme length of the receiver of the pump. The rod having been introduced into the tube, and a magnetic index on the top of it, the end of the tube was sealed up. When now the tube was subjected to high pressure, the material of the tube was compressed and diminished in volume in every direction, and of course therefore in its length. The rod, however, in the inside not being exposed to extra pressure, maintained its original length. The index having been brought down home on the top of the rod before exposing the system to pressure, was kept in its place by the rod, and the tube on the outside was therefore pressed down past it to a certain extent. When the pressure was relieved, the tube recovered its length, and slightly lifted the index. The extent to which the index was free above the rod when that pressure was relieved measured the linear compression of the glass; and multiplying that by three, we had the cubical compression. The results obtained by these means were too rough to be quoted as of any particular value, because measurement of this distance was effected simply by the eye on the scale of millimeters, which was etched on the tube, but with an apparatus I have since had constructed I expect to obtain results of great accuracy, not only for glass, but for other solids.

I shall now direct your attention to a subject of a somewhat more chemical nature, namely, the atmospheric contents of the sea-water. The carrying out of these investigations was one of the principal objects of having a chemical laboratory on board the ship, and that we were able to do so successfully I owe in great measure to the fact of having met Professor Jacobsen, the chemist who was in the Prussian expedition to the North Sea in the year 1872, who very kindly showed me all the apparatus which he was using, and especially his adaptation of Bunsen's method of boiling nitrogen and oxygen out of the water, which was of the greatest value; in fact it made the operation possible on board ship, which otherwise it would not have been.

In order to boil atmospheric gases, that is to say oxygen and nitrogen

(because in sea-water carbonic acid may almost be said to belong to the fixed constituents, as it is quite impossible to eliminate it in the ordinary way *in vacuo*), the general arrangements of Bunsen's apparatus was used. The apparatus has been fully described by Professor Jacobsen, in the *Annalen der Chemie und Pharmacie* for May, 1873. Its speciality consists in the means of making and breaking connection between the flask and the glass tube destined to receive the air eliminated from the water. The water from the bottom was usually collected in the so-called "slip" water-bottle, which has been described by Professor Jacobsen. Water from intermediate depths is obtained in an instrument represented in section in Fig. 5. It is made entirely of brass, which, however, might advantageously be nickel-plated. It consists of a cylinder A, terminated at both ends by similar stopcocks, B, B, which are connected by the rod C. This rod carries, near its upper extremity, a piece of stout sheet brass (D), 10 centimeters long by 15 broad, soldered to the casting, E, which is movable about the axis *e*. The function of this part of the apparatus will be more easily explained by describing the manipulations necessary when collecting water.

FIG. 5.



When intermediate water is to be obtained, the water-bottle is firmly attached to the sounding line, which carries at its end usually a 56lb. or 1 cwt. lead; the stop-cocks are then opened, giving them, with the rod C, the position represented in the figure. The line is then lowered carefully by hand, until the water-bottle is close to the surface, when it is let go, and the line allowed to run out without a check. During its passage downwards, the water courses freely through it, being considerably assisted by the conical end-pieces, K, K. When the requisite depth has been reached, the line is checked, hauled in a few fathoms, then let go, checked again at the same mark, and finally hauled in altogether by the donkey-engine. When the line is hauled in at first, the flap D falls down into a horizontal position, when it is caught by the movable piece of brass F, which moves round an axis *f*, and is supported on the side opposite to E, by the rod G, which rests on the spiral spring H. The water rushing past D when thus in a horizontal position, exercises a sufficient pressure upon the rod to close the stopcocks B, B. When the speed with which the bottle is hauled through the water is increased, the pressure on D becomes so great, that it overcomes the tension of the spring H, and E passes the catch

F, when the rest of the journey upwards is performed with the flap D hanging down, and therefore offering the least possible resistance to the water. The object of at first hauling in only a couple of fathoms or so, and letting the line go again, is to ensure the cocks being closed. For, supposing after the first hauling in they were not quite closed, by letting the instrument descend through the water, the flap D sets itself again, and, on heaving in, it shuts down the stopcocks, which were before but partially closed; or, if they were closed before, it only shuts them the tighter. When the water-bottle has been brought up, it is only necessary to substitute for the lowermost brass funnel, a small nozzle, when the water may be tapped into any vessel destined to receive it. This done, the bottle may be at once lowered to any other required depth, much time being spared by not having to detach it each time. At the upper end of the bottle a small spring safety valve L is introduced, in order that the considerably denser water from below may be able to make room for itself as the surface is approached. In order that the instrument may properly do its work, it is evident that first the stopcocks should be so stiff, that the weight attached to their levers be not sufficient to close them, and secondly, the spring H should be so strong as to ensure the shutting of the cocks before it itself gives way. These conditions are secured by the following means of adjustment. The stopcocks can be made stiffer in the usual way, by tightening the screws which secure the "keys" in the barrels; the tension of the spring H can be increased or diminished by means of a screw at the lower end of the tube containing it; and the mobility of the stopcocks can be further regulated by means of the screws M, M. Although from this description, the operation of adjustment may appear complicated, it is, in fact, practically, very simple. After the first time of use, it is rare that any further adjustment is required than a turn of the screws M, M.

The diameter of the apertures at either end is necessarily smaller than that of the cylinder, it is therefore impossible for the water in it to be entirely changed while descending through a distance equal to its own length. It became a question, therefore, for experiment to decide what actually was the rate of change of water. To this end, a few experiments were made in a fresh-water lake. The bottle being filled with water containing some yellow prussiate of potash, was sunk in the lake, until the surface of the water was on a level with the upper stopcock, when the stopcocks were opened, and the line let go. On being brought up again, the contents were tested with solution of perchloride of iron. It was found that when the bottle had been sunk to a depth of a fathom and a half, the water had been entirely changed, the iron solution being wholly without action on it. We may be certain, then, that the water which we obtain by this means is an

average of the last two fathoms through which the bottle has passed.

The weight used as a sinker should be chosen so as to impart sufficient velocity not to lose time unnecessarily over the operation, and at the same time not to give an excessive velocity at the depth where the water is to be collected, because the rate of change of water depends on the friction of the water inside the bottle, and so on the velocity of descent. In practice, for depths over 100 fathoms, a weight of 112 lbs. was used, and for depths from 25 up to 100 fathoms, a weight of 56 lbs. was used. For less depths, the weight of the bottle itself was sufficient. The velocity of descent at the depth where the water is to be collected, should not exceed twelve feet per second. The mean velocity of descent for the interval between 75 and 100 fathoms from the surface was, with 56 lbs. nine feet, and with 112 lbs. eleven and a half feet per second.

When once let go, it is essential that the line should run out to the required depth without a check; it is then, however, immaterial, as far as the water-bottle is concerned, what interruptions occur in heaving in. The fulfilment of the condition of running out without a check never presented any difficulty on board the "Challenger," depending as it does on the care of those who tend the line. When, however, by accident a check does occur, the line is stopped, and the water-bottle brought up again, reset and sent down again. In order to utilise any such accidents, it is usual to take the water from the greatest depth first; then if a check does occur, it may occur at one of the desired intermediate depths, and so no time would be lost. In designing the water-bottle, it had been my intention to use it not only for collecting water, but also as a flask, so that the atmospheric gases could be boiled out of it without transvasing the water. In practice, however, I have not been able to get air-tight stopcocks, besides which, it would make an inconveniently large apparatus in a very small laboratory. I have spoken of this water-bottle as being only used for intermediate waters, but there is no reason why it should not be used for bottom water; indeed, where the sounding lead does not weigh over 1 cwt., it is frequently used for this purpose. In the case of deep soundings, however, where a weight of three, and sometimes four hundred-weight is used, the "slip" water-bottle is always preferred.

When the water-bottle has been brought up full of water, the lower funnel is unscrewed and a nozzle put in its place, with a long glass tube attached to it. This tube reached to the bottom of the flask, and by it the water was run into the flask as carefully as possible without allowing any bubbling or unnecessary commotion in the water. The necessity for transvasing the water before boiling, is a defect in the method. When, however, it is carried out expeditiously and carefully,

it does not appear to introduce any serious error into the results. As a proof that this is so, I may mention that one sample of water brought up by this instrument from a depth of 2,800 fathoms, contained only 3 per cent. of oxygen; and a sample of rain-water which I collected on one occasion had less than 1 per cent. of oxygen. In transvasing, the flask was filled up to the lip and usually allowed to run over for a little, so that the upper layer of water which had been most in contact with the air might be eliminated. The connections with the receiving tubes were then made. The water in the small bulb was kept boiling vigorously for from 10 to 12 minutes before the upper end of the gas tube was closed with a glass rod and sealed up. When this was done, connection was established between the flask and collecting apparatus, the gas in the water immediately beginning to be evolved. The lamp was now lighted below the water-bath which contained the flask, and the temperature of the water thus raised until the water in the bath boiled; this was continued always for an hour, usually for an hour and a-half, and often longer, the exact duration of the boiling depending on the nature of the other work going on.

Although disadvantageous as regarded comfort and ventilation, the lowness of the roof in the laboratory presented some advantages especially for fixing apparatus. It will be evident that the apparatus with which we are at present dealing possesses a good deal of spring. In order to give it more rigidity, the upper extremity of the brass rod supporting the gas tube was supported by strings from the roof.

As the amount of oxygen and nitrogen contained in a litre of sea-water may amount to 22 or 23 c.c., it is advisable that the gas-tubes used for collecting it should not have less than 50 c.c. capacity, in order that the water may continue to boil vigorously when the flask is immersed in the water-bath. As long as this is the case, the water in the small bulb has no opportunity of cooling, and so choking the tube. The gas-tube itself, however, should not be unnecessarily heated.

The rolling of the ship (otherwise an annoyance) was here not altogether disadvantageous. It produced a species of pumping in the apparatus, so that when the boiling was getting sluggish, a heavy roll was enough to start it again.

The apparatus for the determination of the carbonic acid is described by Professor Jacobsen in the memoir above cited. The alterations which I introduced into it were not of an essential character, and were suggested by exigencies of locality. In principle, the method consisted in distilling to dryness a measured volume of the water in a current of air free from carbonic acid. In the receiver and in the tubes interposed between it and the aspirator, a measured quantity of baryta-water of known strength was placed. The baryta removed

from this solution in the course of the experiment was a measure of the carbonic acid eliminated from the water. It is well known that sea-water retains its carbonic acid with great tenacity, mere boiling having but little effect on it. Amongst the experiments which occupied me during nine months previous to my receiving the appointment of chemist in the expedition, with a view to settle on a trustworthy basis the programme for the chemical work during the expedition, was a thorough investigation of the behaviour of sea-water to carbonic acid. These investigations showed that the dissolved sulphates were amongst the most energetic agents in the retention of the carbonic acid. From this I concluded that if the sulphates were removed, the carbonic acid would come away more easily. Consequently, before beginning to distil the water for determination of the carbonic acid, about 15 c.c. of a saturated solution of chloride of barium were added to it. The flask having been closed was shaken so as to mix the solution.

This no doubt had to a certain extent the desired effect of assisting the disengagement of the carbonic acid from the water boiling at ordinary pressure, although when half of the water was distilled there was still a notable amount (about one-tenth of the whole) in the residue; but it had no effect in rendering it more amenable to the action of reduced pressure. It had a very useful effect in eliminating "bumping" altogether, even when the distillation was carried to complete dryness. A liquid residue of about 10 c.c. was usually left in the flask. The baryta remaining in the solution was determined by means of hydrochloric acid, rosolic acid being used to determine the point of neutralisation.

The results obtained are put shortly in the table (p. 462). Of the gas samples which were boiled out in the Bunsen apparatus, I was enabled to analyse about a third before my connection with the expedition ceased; the remainder, as far as I know, have not yet been analysed. The results are therefore subject to correction from future experiments. The mean value of the oxygen per cent., that is oxygen and nitrogen being put as 100, is 33·67. Jacobsen experimenting in the North Sea, found a mean of 33·9, and observed a variation between the limits of about half per cent.; that is to say, he observed from 33·7 to 34·2 per cent. of oxygen in the mixture of oxygen and nitrogen, and he came to the conclusion that this was a real difference, and not due to any errors of observation. My observations, which extend over a much greater area, give a lower average, 33·67, and a very much greater variation in the individual results, in round numbers from 33 to 35 per cent.

The amount of oxygen obtained in samples in the Antarctic regions is usually very much higher than in the moderately warm regions

Depth. Fathoms.	Carbonic acid. Grams in 1 litre.	No. of determinations of CO_2.	Oxygen per cent. (N + O = 100).	Nitrogen. c.c. in 1 litre.	Average temperature of water.	Nitrogen according to Bunsen.	Deficiency of nitrogen.	Oxygen. c.c. in 1 litre.
D.	C.		$100 \cdot \frac{O}{N + O}$	N.	T.	N'.	N'—N.	O.
					°C.			
Surface.	0·0426	73	33·67	—	—	—	—	—
25	0·0337	2	33·36	—	—	—	—	—
50	0·0488	10	32·33	—	—	—	—	—
100	0·0436	5	30·21	11·26	14·6	11·75	0·49	4·24
200	0·0446	8	23·40	11·71	13·0	11·92	0·21	3·59
300	0·0440	4	11·37	13·00	6·9	13·45	0·45	1·67
400	0·0411	10	15·46	13·10	5·1	14·00	0·90	2·41
800	0·0422	7	22·62	13·86	2·5	15·00	1·14	4·06
over 800	0·0446	7	23·45	14·37	1·5	15·40	1·03	4·40
Bottom	0·0474	54	—	—	—	—	—	—

about the trade winds; and also in all the warm regions. In the Antarctic regions I found as much as 35 per cent., and as low as 32·9 per cent. in the trade wind regions. The number of observations is, however, as yet too small to admit of general conclusions being drawn from them.

The results obtained at other depths are given in the table. I have not taken a mean of the bottom ones, because the depth and other conditions were too various to make it of value.

Looking at the oxygen percentages dissolved in water at different depths, we see that they diminish with considerable rapidity as the depth increases, until a minimum is reached at about 300 fathoms, after which it slowly increases.

The percentage in very deep water appears to depend a great deal on the geographical position, being the greater the nearer it is to a position where the surface-water at some period of the year has the same temperature. This appears certainly to hold in the southern hemisphere. In the northern my observations on bottom water are from the Pacific, where there is without doubt a considerable admixture of southern cold water, which is therefore very remote from its source, and which therefore, mixed with the cold northern water, gives a result below what we find in similar southern latitudes. I believe the prevalent opinion attributing the low temperature in the deep waters of the North Pacific *entirely* to a southern source to be quite erroneous. In the northern parts of the Pacific the winter tempera-

ture is quite low enough, and the differences of temperature at the same place at different seasons, and in different places at the same season, are quite sufficient to cool down a large area of the northern Pacific, and when the remainder (the larger portion) of the air samples which I boiled out have been analysed, much light will no doubt be thrown on the question.

Whatever view we may adopt as to the cause of ocean circulation, there can be no doubt that the actual effect is to cause on the whole a rise of cold water towards the surface near the equator. This water has been impoverished since it was last exposed to the atmosphere, and would probably not contain more than 15 or 20 per cent. of oxygen in its absorbed atmospheric air. This percentage being so remarkably reduced at 300 fathoms shows the existence of a powerful reducing agent at that depth, and as we know from Mr. Murray's observations that life generally is remarkably abundant at these depths, it is a fair inference at least provisionally to assume that the disappearance of oxygen is due to the abundance of life. It must be remembered, however, that our observations were made in tropical equatorial waters, where surface aëration is hindered by the constant high temperature of the atmosphere. In colder regions we have every reason to believe that the aëration is much more energetic. Unfortunately in dealing with sea-water the amount of carbonic acid present affords no means of controlling the amount of oxygen which is deficient.

In distilled water carbonic acid is absorbed according to well-known laws, but this is not the case with sea-water, for which the laws have yet to be investigated.

The amount of carbonic acid per litre in water at the surface, according to an average of a great number of observations, was 42·6 milligrams. The highest average amount, 48·8, was at 50 fathoms, falling to 41·1 at 400 fathoms, and rising to 47·4 at the bottom.

It will be seen from the table that the absolute amount of carbonic acid dissolved is very great, and that the variations with depth are insignificant. Observations at the surface showed that, on the whole, less carbonic acid was present in warm than in cold water, but no law was apparent. We know from other investigations that the saline contents exercise a very strong influence on the amount absorbed, and there are other causes which introduce seeming irregularity into observations of this kind.

There is a remarkable difference in the results which I have obtained in the open ocean and those obtained by Dr. Jacobsen in the North Sea. I have found approximately 45 milligrams per litre as a mean amount. Jacobsen found 88·6 milligrams, or about exactly double the quantity. It is difficult to imagine to what cause so great a discrepancy is to be attributed if it does not depend on the nature of the

University of Michigan

water. The water in which nearly all my observations were made was the deep clear ultramarine-blue water of the ocean. The North Sea water in which Jacobsen experimented is comparatively opaque and green. In the Antarctic Ocean, where such water was met with occasionally, though very sparingly, the carbonic acid was always present in marked excess. The green colour of shoal water is generally attributed to the influence of solid matter, which may also tend to retain carbonic acid, as we know is the case with dissolved saline matter. The subject is worthy of investigation; and as sea-water collected well out at sea contains, as far as I have been able to observe, no appreciable amount of putrescible matter, and as the carbonic acid dissolved has no tendency to escape at ordinary temperatures, samples, if carefully collected and preserved in clean stoppered bottles, would be in a perfectly fit state for examination after a long voyage.

In the Table at page 462, we have seen the distribution of gaseous contents at different depths. In the Table below we have the mean results from different zones of bottom water. It will be seen that the highest percentage of oxygen, as well as of nitrogen and carbonic acid, is met with in Antarctic regions, and that the amount of all these bodies present in the water diminish as we approach equatorial regions.

Bottom Water.

Latitude.	Oxygen per cent. O + N = 100.	Carbonic acid per litre. Grams.	Nitrogen. c.c. in 1 litre.
66° S. to 35° S.	27·63	0·0518	13·73
35° S. to 10° S.		0·0466	
10° S. to 10° N.	21·85	0·0409	11·71
10° N. to 35° N.		0·0459	
35° N. to 38° N.	20·76	0·0426	12·91

The absolute maximum of carbonic acid in bottom water was observed at the highest southern latitude where observations were made, namely, 0·0829 gram per litre in lat. 65° 42′ S., long. 79° 49′ E., and 1,675 fathoms. The minimum amount in this zone was 0·0385 gram per litre in lat. 48° 37 S., long. 55° 17′ W., and 1,035 fathoms. Between 35° and 10° S. latitude I have analysed only one air-sample from bottom water. It was collected lat. 12° 45′ S., and long. 147° 1′ E., in a depth of 1,700 fathoms, and contained 17·4 c.c. of oxygen and nitrogen in one litre, 20·97 per cent. of which was oxygen, and 0·0609 gram CO_2 in a litre.

In this part of the ocean, which has been called the Melanesian Sea, I observed some anomalous results. Amongst them may be reckoned the above very high percentage of carbonic acid. The amount varied

greatly at different stations. In lat. 14° 7′ S., long. 153° 43′ E., and 2,450 fathoms, it was 0·0434 gram, and in 1,400 fathoms, close to Raine Island, it was 0·0361. Both the maximum and the minimum amounts were found over "globigerina ooze," while the medium (0·0434) was found over "red clay." At the surface, too, in lat. 17° 25′ S., long. 169° 5′ E., there was found in one litre 0·096 gram carbonic acid, 14 c.c. of oxygen and nitrogen, of which 32·35 per cent. was oxygen. The temperature of the water was 25·8° C., and, notwithstanding, it contained the greatest amount of carbonic acid observed in any water during the cruise, and also the least oxygen percentage of surface water.

At other stations in the same sea 0·0317 and 0·0357 gram carbonic acid were observed. Only one air-sample, however, has as yet been analysed. Again, in the same zone, but to the north of New Guinea, a very large amount of carbonic acid was met with in the bottom water, though the surface water was not abnormal in this respect. In lat. 4° 19′ N., long. 130° 15′ E., and 2,500 fathoms, 0·0524 gram carbonic acid was found, and in lat. 5° 31′ N., long. 145° 13′ E., and 2,325 fathoms, 0·0619 gram carbonic acid was found in one litre. In the Celebes Sea 0·0524 gram carbonic acid and 21·78 per cent. oxygen were found. In the Sulu Sea the carbonic acid is 0·0243 gram, and the oxygen percentage 29·63. The deep water in this sea has a temperature not below 10·2° C., so that it is in many respects peculiar; under these circumstances, however, it is remarkable that there should be so little carbonic acid and so much oxygen.

We see, then, that in this zone there is very considerable fluctuation in the gaseous contents of the sea-water, especially at the bottom. In the zone from the parallel of 10° to that of 35° N. latitude, there is an analysis of only one air-sample from the bottom. It is from the deepest sounding from which bottom has been obtained, namely, 4,475 fathoms in lat. 11° 24′ N., and long. 143° 16′ E. Here again we have a very small quantity of carbonic acid (0·0312 gram), and of nitrogen and oxygen (13·9 c.c.), with a high oxygen percentage (29·11). As the depth reached on this occasion was quite unexpected, the sounding was repeated with substantially the same result as regards depth, but the water-bottle came up the second time unclosed, so that the attempt to verify or control the somewhat abnormal results obtained from water from such exceptional depth was frustrated in the most annoying way possible. The water-bottle was that commonly used for bottom water, which is constructed to close on touching bottom. The "tumbler," which by falling forward disengages the cylinder which encloses the water between suitable valves, had in this case fallen backwards, thus, as it were, choking itself. In this zone the maximum carbonic acid was 0·057 grams in lat. 19° 4′ N., long. 65° 7′ W., and

3,875 fathoms, being the deepest water found in the Atlantic. The minimum carbonic acid was that above referred to as having been found in the Pacific in the deepest water attained during the cruise, with the exception of this last. All the observations in this zone are from the North Atlantic, where the conditions are in many respects exceptional. The saltness is much above the average, and it is therefore not astonishing that the carbonic acid should also be comparatively high.

To the north of 35° N. latitude the observations are principally in the Pacific, the mean amount of carbonic acid observed being 0·0426 gram per litre. The two highest results (0·064 and 0·0536 gram) were observed in the North Atlantic. If these are eliminated, the mean amount in this zone of the Pacific is 0·0361 gram. The absolute amount of oxygen and nitrogen is higher in this zone than in the equatorial one. The amount of nitrogen is 12·91 c.c. per litre. In the same latitude in the South Atlantic two observations give 14·01 and 14·76 c.c. per litre. If the bottom water in this zone of north latitude were made up of equal parts of water prepared in the southern and in the northern hemispheres, the mixture would probably contain nitrogen in the quantity above quoted.

Amongst the air samples collected from intermediate depths, those from 800 fathoms present a remarkable uniformity in the oxygen percentage. The results are given in the following table:—

Latitude.....	32° 36′ S.	37° 47′ S.	35° 45′ S.	3° 10′ N.
Longitude.....	137° 43′ W.	30° 20′ W.	18° 31′ W.	14° 51′ W.
Oxygen percentage	22·65	22·95	23·25	22·22
Nitrogen c.c. per litre ...	13·72	14·10	15·81	11·82
Oxygen c.c. per litre	3·88	4·20	4·79	3·38

The first three samples are from southern latitudes, between the parallels of 32° and 38°, and the fourth is from a position close to the equator in the Atlantic. It will be seen that the oxygen percentages are much more uniform than the absolute amounts of that gas per litre of water. Indeed, if we compare the first and the last columns, we see that the equatorial Atlantic water possesses absolutely much less oxygen than the North Pacific water, though its percentage is higher. The amount of nitrogen present is also very variable. In the South Atlantic we have as much as 15·81 c.c. per litre, while at the equator in the same ocean there is only 11·82 c.c. The temperature of the water in all the cases was practically the same, being from 2·5° to 3° C., and the specific gravity was similar, in the two extreme cases identical. This disappearance of nitrogen is very remarkable. Humboldt and Provençal (*Mém. d'Arc.*, ii, 377), in their investigations on the respi-

ration of fishes, noticed a similar phenomenon, nitrogen always disappearing side by side with the oxygen, though in no constant ratio to it. They experimented on tenches, letting them remain in the water until they were uneasy, then boiling out the water. They found that a tench will exhaust the oxygen in a cubic meter of river-water in 21 months. They observed the oxygen percentage (N + O = 100) reduced as low as 1·3, and observed that want of oxygen affected the fish more than the presence of excess of carbonic acid.

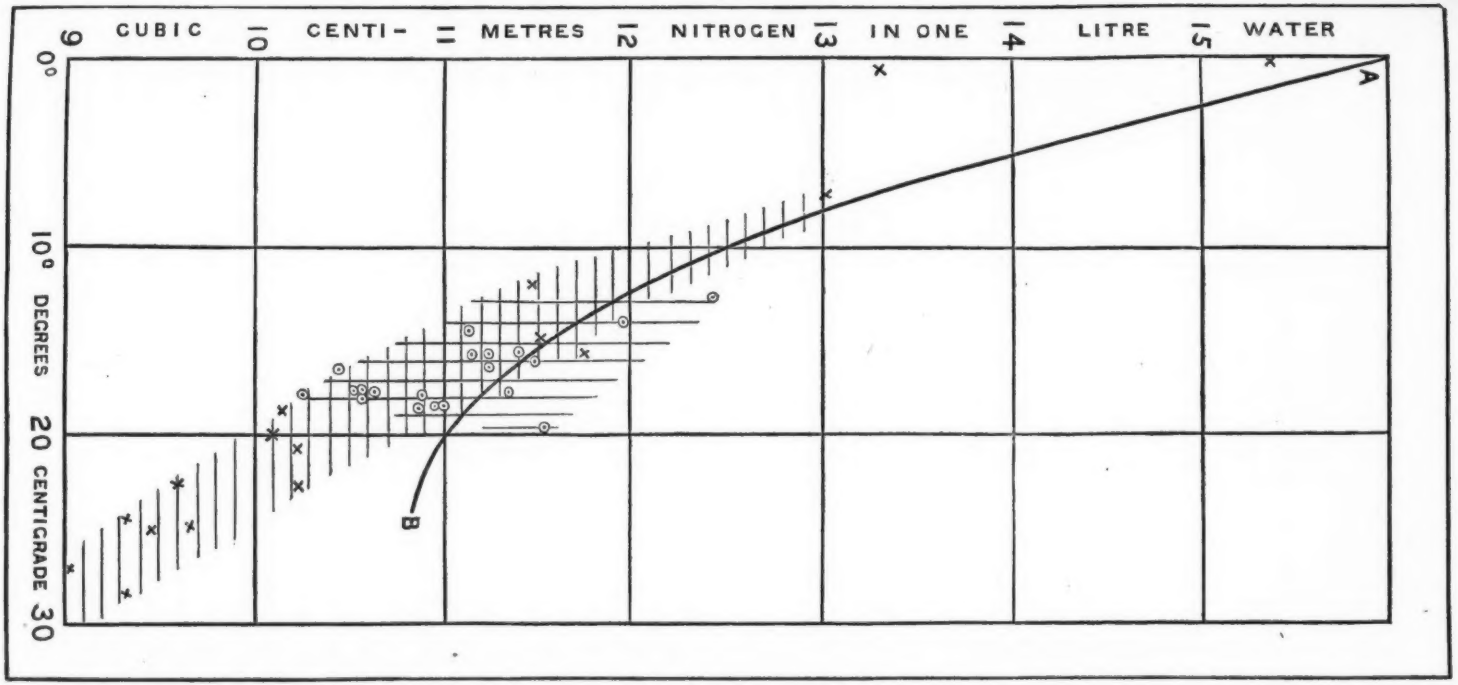
The lowest oxygen percentage observed was 3·84, in water fetched 75 fathoms above the bottom, in lat. 30° 22′ N., long. 154° 56′ W., the depth of the sea being 2,950 fathoms. The absolute amount of oxygen was 0·6 c.c., and of nitrogen 15 c.c., so that there was no deficiency of nitrogen.

While becalmed off the north coast of New Guinea, I boiled out the air from rain-water collected as it ran off the awning. The temperature of the rain so collected was usually from 23° to 24° C., and in order not to interfere with the work of the day, it was kept in perfectly full bottles over night and boiled the next morning. Three rain-waters were so treated, and the oxygen percentages found were 18·56, 25·42, and 0·52, and in the last two were found 11·27 and 11·66 c.c. nitrogen per litre. There was therefore rather more nitrogen than would have been expected from the temperature. The amount of oxygen present, however, varied in the most extraordinary manner, the last sample being almost completely deprived of oxygen. If the carbonic acid be reckoned as oxygen, we obtain the following percentages in the same order, 28·45, 30·83, and 25·68. The rain-water when freshly collected remained perfectly clear on addition of baryta-water; the carbonic acid had therefore been entirely formed during the night at the expense of the oxygen dissolved in the water. There must therefore have been also a considerable amount of easily oxidisable carbon in the water, and in fact I collected a considerable quantity to be used for the preparation of standard solutions, but could make no use of it, as it speedily produced a fungus-like deposit. Some also which I tested for ammonia continued to give it off on distillation almost to dryness; and the water remaining in the retort reduced permanganate energetically. At the time I did not know of the deficiency of oxygen, and I attributed the organic matter to contamination from the awning, although the explanation never fully satisfied me, because the amount of rain which fell was sufficient to thoroughly wash the awning, and as it did not answer the purpose for which I had particularly collected it, I reverted to the ship's distilled water, which was always of excellent quality. It will be seen that the carbonic acid does not completely cover the loss of oxygen; no doubt, however, some water was formed, and it is not

impossible that sulphurous acid from the furnace gases escaping by the funnel may have had some reducing effect.

The determinations which were made of the absolute amount of these permanent gases, as we are accustomed to call them, in the litre, have been plotted in Fig. 6. The curve represents Bunsen's curve of the absorption of nitrogen in distilled water. The ordinates represent cubic centimeters of nitrogen absorbed by distilled water of different temperatures when exposed to the atmospheric mixture of nitrogen and oxygen. The results obtained by boiling the gases out of the surface water have been plotted on the same figure, and also those obtained by Jacobsen in his experiments in the North Sea, in order to see how they would fall in with the curve already found for distilled water. I have found it was impossible either to get my own results or Jacobsen's to agree with this curve. With hardly an exception all the observations fall below the curve. About 10° to 12° C. they nearly coincide with it, but both at lower and higher temperatures, and especially at higher temperatures—and my own experiments were made to a great extent in water of higher temperatures—fall very considerably below it. The shading covers the whole of the experiments, so that it shows at a glance how the experiments agree with the curve. We see at once that above 20° C. they depart very markedly from the law indicated by the line A B. The strong convexity of Bunsen's curve does not appear to be probable, knowing, as we do, how rapidly all but the very last traces of air are eliminated from water by heat. The curve as indicated by our experiments on sea-water would very much more nearly approach a straight line; it would, however, have a slight convexity in the same sense as A B. On this point the analysis of the remaining air-samples which were collected will throw much light, especially as a large number of them are from surface water in the warmest regions of the earth.

FIG. 6.



Cub. cents. nitrogen dissolved in 1 litre sea water at different temperatures. × "Challenger." ⊙ "Pomerania."
AB is the curve according to Bunsen for distilled water at a pressure of $\frac{4}{5}$ths atmosphere.

LVI. *The Action of Alkaline Hypobromite on Ammonium Salts, Urea, and Oxamide.* Part I.

By William Foster, B.A., Lecturer on Chemistry, Middlesex Hospital Medical College.

About two years ago I was called upon to determine the amount of urea in solutions containing other nitrogenous bodies. The hypobromite method being inapplicable in consequence of the solution of nitrogen from nitrogenous bodies other than urea which were present, I was led to study the action of alkaline hypobromite on several well-defined compounds containing nitrogen. Some of the results obtained I now beg to lay before the Society.

Action of Alkaline Hypobromite on Ammonium Salts.

When these bodies in aqueous solution are subjected to the action of the hypobromite, the mixture effervesces briskly, evolving gaseous nitrogen. Knop and Wolf (*Chem. Centralblatt*, 1860, 257) have studied this reaction. In their experiments they obtained the whole of the nitrogen in the gaseous form. They recommend the process, and describe an apparatus for the quantitative estimation of ammonium salts. Abnormal results were obtained with ammonium oxalate.

Dietrich (*Zeit. Anal. Chem.*, v, 40) states that there is a constant loss of 2·50 per cent. of nitrogen in the reaction, and he considers that this proportion of the nitrogen remains dissolved in the solution. Wagner (*ibid.*, xiii, 383) confirms Dietrich as to the percentage of loss of nitrogen. Knop (*ibid.*, ix, 226) states that there is no loss if the solution is not very weak and the nitrogen is not allowed to escape from contact with the hypobromite until the reaction is completed; if this precaution be omitted, the nitrogen will contain undecomposed ammonia, and the results will be too low.

From the ready way in which the nitrogen can be evolved, I was led to hope that Knop's process would be a good and expeditious one. With excessively strong soda-solution freshly charged with bromine, the amount of gas obtained is equal to the theoretical amount of nitrogen in the quantity of ammonium salt operated on. The mean of two experiments on 5 c.c. of a 2 per cent. solution of ammonium sulphate gave 99·7 per cent. of the total nitrogen. Such viscid solutions are objectionable on account of their tendency to envelop air on agitation which is liberated on dilution during an experiment.

The mean of four experiments with the same ammonium sulphate

solution and a slightly weaker alkaline hypobromite solution, gave 95·5 per cent. of the total nitrogen.

With an alkaline hypobromite solution of the strength recommended by Knop, the mean of four experiments gave 93·3 per cent. of the total nitrogen of the ammonium salt.

With hypobromite of Knop's strength and an apparatus for collecting the gas over the hypobromite without dilution, the mean of three experiments gave 92·8 per cent. of the total nitrogen. In these cases no increase in the volume of the gas was obtained by allowing it to remain in contact with excess of the alkaline hypobromite.

A large number of experiments have been made in this direction which lead me to conclude that, with Knop's strength of alkaline hypobromite and the ordinary forms of apparatus, there is a deficiency of about 7 per cent. of the total nitrogen of the ammonium salt.

When the solution of Knop's strength is diluted with an equal volume, or even two volumes, of water, I find that the amount of nitrogen suppressed is practically the same as when the undiluted solution is employed.

The Action of Alkaline Hypobromite on Urea.

This action has been studied by Knop, Russell and West, Dupré, and several other chemists.

When the mean solution is treated with the hypobromite, nitrogen is briskly evolved. When excessively strong soda-solution is employed, nearly the whole of the nitrogen is readily obtained as gas. The mean of two experiments gave 98·0 per cent. of the total nitrogen of the urea, no heat being applied to the vessel, and the gas being measured at the end of 15 minutes. The objection to the use of such viscid solutions has already been noticed.

When the soda-solution is of the strength recommended by Knop (10 grams in 25 c.c. of liquid), there is a deficiency of nitrogen. In their experiments on this subject, Drs. Russell and West employed Knop's strength of solution, and found, from a large number of experiments, that there was a deficiency of 8 per cent. of the total nitrogen of the urea. Their results have been confirmed by several other chemists.

The mean of three experiments with soda-solution of about the normal strength gave me 92·3 per cent. of the total nitrogen at the end of 15 minutes without the application of heat.

A large number of experiments have been made with various strengths of hypobromite solution, which show that with the stronger solutions there is a greater yield of nitrogen than with the weaker ones,

and that with normal solutions there is a deficiency of about 8 per cent. of the total nitrogen.

Action of Alkaline Hypobromite on Oxamide.

In some unpublished experiments of Dr. Russell's, this reaction has been briefly studied. When oxamide is added to the alkaline hypobromite, decomposition at once commences, is attended with a brisk evolution of nitrogen gas. In consequence of the light and insoluble character of the oxamide, it is advisable to employ a vessel which admits of being easily agitated. If the agitation during decomposition be neglected, some time is required before the last portions of oxamide disappear. The strength of the alkaline hypobromite is a matter of some importance. When the hypobromite is of the normal strength, the decomposition progresses slowly, even on the application of heat, and at the end of some minutes there are generally small quantities of white powder still remaining, which is no doubt unaltered oxamide. When the freshly prepared normal alkaline hypobromite is diluted with about an equal volume of water and then subjected to the action of the oxamide, the mixture effervesces readily on agitation, giving off gaseous nitrogen, whilst the temperature of the vessel rises in a very marked degree. This elevation of temperature facilitates the decomposition of the oxamide, and generally results in a perfectly bright solution at the end of four or five minutes. In some cases, it is advisable to apply heat to the containing vessel in order to complete the reaction. In the presence of excess of the hypobromite no odour of ammonia can be detected.

The experiments for determining the amount of nitrogen evolved as gas, were made in the form of urea apparatus, such as has been suggested by Dupré and Apjohn. This consists of a small test-tube attached to the lower side of an indiarubber plug which accurately fits the neck of a small flask. Through the plug passes a piece of glass tubing attached to a graduated receiver for collecting and measuring the gas evolved in an experiment. The oxamide having been weighed, is placed in the test-tube, and a small quantity of water added. The freshly prepared hypobromite solution is then placed in the flask and the plug with attached tube containing the oxamide is then inserted, and the whole apparatus left for a few minutes to assume the temperature of the apartment, the level of the water in the measuring-tube being afterwards carefully adjusted. All being now ready, the flask is gently tilted and shaken alternately, so as to cause the admixture of the oxamide and hypobromite, the receiver at the same time being gradually raised so as to keep the level of the water inside and outside the measuring tube as nearly equal as possible.

When the decomposition is complete, which is known by the solution being perfectly bright, and still having a distinctly yellow colour, the whole apparatus is cooled down to the original temperature, and the increased volume of gas in the tube is determined. This number is then corrected in the ordinary way for temperature and pressure.

The following four experiments are illustrations of the experimental numbers which have been obtained :—

Oxamide taken in grams.	c.c. of gas evolved uncorrected.	Percentage of nitrogen obtained from oxamide as gas.	Percentage of total nitrogen of oxamide evolved as gas.
·245	51·00	24·3	76·0
·222	44·75	23·5	74·0
·247	52·00	24·0	75·5
·201	40·25	23·5	74·0

The mean of the four experiments gives 74·87 as the percentage of the total nitrogen which can be obtained in the gaseous form in this way. Oxamide contains 31·8 per cent. of nitrogen.

After satisfying myself of the perfectly regular yield of nitrogen under these conditions, attempts were made to ascertain the state of the suppressed nitrogen, amounting to 25 per cent. of the total quantity present in the original oxamide. The perfectly bright solution at the close of an experiment on the amount of gas evolved was then transferred to a large clean flask containing a considerable quantity of the "copper-couple," and distilled. Ammonia appeared in the condensed liquid very slowly, so that on distilling for three or four hours and collecting about 300 c.c. of distillate, not more than one quarter of the suppressed nitrogen could be accounted for. On allowing the flask and its contents to stand over night and commencing the distillation in the morning, the first portions coming over were relatively richer in ammonia than those of the previous day. Ammonia continued to come over after distilling for three or four hours on the second day of the experiment, and owing to the fracture of the flask towards the close of each of several experiments, I have not yet pushed the distillation far enough to yield me a distillate free from ammonia. However, I have recovered more than two-thirds of the suppressed nitrogen as ammonia, and I have no doubt that the whole of it can be recovered in this way.

Operating on ·223 gram of oxamide, I have obtained ·0124 of nitrogen as ammonia, the amount to be accounted for being ·0177.

The slow reduction of the nitrogen compound by the copper-couple in a boiling alkaline solution led to the belief that it existed as a

nitrate. Some of the sodium hypobromite was then treated with an insufficiency of oxamide, evaporated to dryness, fused and kept in that condition for some minutes. The fused mass was then dissolved in water and starch-solution, iodide of potassium, and tartaric acid added in excess. Under these circumstances an intense blue colour was always produced.

The soda employed in these investigations was purchased as that made from metallic sodium, but experiments made to test its purity show that it contained traces of something which yields excessively minute quantities of ammonia when boiled with the copper-couple. When converted into hypobromite, fused, and afterwards treated with starch-solution as above, the results have been generally negative, but not uniformly so. I am therefore at present unable to state the precise condition of the suppressed nitrogen. The experimental evidence is in favour of the notion that it is converted into nitrate, whilst, from general considerations of the decomposition-products of oxamide, one would rather expect to find it in the condition of cyanate. This latter view finds further support in the experiments recently made by Mr. Fenton, who has found that a portion of the nitrogen of urea is converted into cyanate, under somewhat similar circumstances.

I am not inclined to regard the evolution of three-fourths of the nitrogen of the oxamide as accidental, the result of a particular strength of alkaline hypobromite only. The results obtained would rather favour the view that all the nitrogen in the oxamide molecule is not similarly situated, and in depicting the behaviour of oxamide in this reaction, I would suggest the formula—

$$C_4\begin{cases}(NH)_3\\NHHO.\\(HO)_3\end{cases}$$

It is my intention to have some pure sodium hydrate prepared, and then settle the most interesting part of this inquiry—the condition of the suppressed nitrogen in the experiments described.

I also propose investigating the action of hypobromite on acetamide and other bodies.

LVII.—*On the Part played by Carbon in reducing the Sulphates of the Alkalis.*

By James Mactear, of St. Rollox Works, Glasgow.

The action when an alkaline sulphate, such as the sulphate of soda, is reduced by carbon, although investigated by such men as Liebig, Gay-Lussac, Berthier, Berthollet, and Vauquelin, has been a much misunderstood subject.

The general idea that the decomposition was a simple change of elements resulting in the formation of sodium sulphide (Na_2S), though seductive, has been shown by experiments made from time to time to be insufficient.

In a series of documents which have been entrusted to me by Mr. John Tennant, of St. Rollox, the late Professor Liebig describes at length a process which he had invented for the production of carbonate of soda. His letter announcing his discovery is dated 11th July, 1839, and his process was founded, as he himself says, on a discovery of Gay-Lussac's, that "caustic potash heated with wood sawdust, gave off *pure hydrogen*, and produced oxalate and acetate of potash. These two salts, if heated to redness, are converted into carbonates, the formation of oxalic and acetic acid taking place from the decomposition of water, the oxygen of which combines with the carbon while the hydrogen goes off":—

"Proceeding from this, and considering the great alkalinity of sulphuret of sodium, I thought it ought to have the same action upon wood fibre, that is, by heating a concentrated solution of this sulphuret with sawdust, there ought to be, at a certain temperature, the formation of oxalate and acetate of soda, and the evolution of sulphuretted hydrogen.

"This is exactly what takes place at 200° C. Heated to 300° C. these two salts are converted into carbonates."

Liebig says that he "had submitted this process to the judgment of the greatest chemists, and Gay-Lussac thinks it the most rational, and at the same time most simple process for producing carbonate of soda, and for using the sulphur." And again, in the same communication, he says, "In the opinion of Gay-Lussac and Berzelius this process will entirely supersede the present method."

The late Professor Graham had the process submitted to him, and reported to Liebig, "Your new experiment I have carefully repeated, and I do hope great things from it."

Gay-Lussac tried the process at Chauny on a very extended scale.

These experiments, and also a series conducted in St. Rollox Works, proved the process to be a failure as a method of manufacturing carbonate of soda, and it was abandoned; but Liebig, in reasoning on the causes of failure, seems to have been led to believe that it was owing to the decomposition of sulphate of soda by carbon being much more complex than had been thought, and he formulated the action as being—

$$2Na_2SO_4 + 4C = Na_2CO_3 + Na_2S_2 + 2CO_2 + CO.$$

(This formula has been altered into new notation for more convenient comparison.)

Unger, however, further examined the subject at Liebig's request, and seems to have decided that the decomposition of sulphate of soda by carbon resulted in—

$$Na_2S + CO. \quad \text{Thus:—} Na_2SO_4 + 4C = Na_2S + 4CO.$$

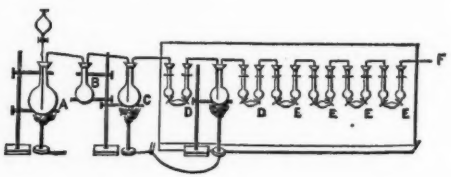
But he again, in the second part of his memoir, examines the subject, and modifies his views so as to assume that it was—

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

My own investigations made at various times had led me to be dissatisfied with the explanation of what at first sight seems a very simple decomposition, and with a view of elucidating the question, I have made a series of experiments, the results of which I have now the honour of laying before the Chemical Society.

The method of conducting the experiments was as follows:—

The sulphate of soda thoroughly dried, and (a lamp-black which on examination proved to be remarkably pure) carbon thoroughly ignited and cooled out of contact with air under a desiccator, were mixed as rapidly but thoroughly as possible, and placed in a platinum crucible covered with a tight-fitting lid; this was then heated by gas in a jacketed support: after heating it was cooled under a desiccator and weighed. The crucible, with its lid and contents, was then placed in a flask fitted with a stopcock funnel and evolution tube, connected with a series of absorption vessels:—



A, evolution flask: B, trap flask containing a small quantity of dilute HCl; C, C, flasks containing a solution of As_2O_3 in HCl; D, D,

are absorbing tubes containing the same solution of As_2O_3 in HCl; E, E, E, E, are absorbing tubes containing solution of barium and sodium hydrates; F is an exit-tube leading to the Bunsen pump.

The crucible and contents having been placed in the evolution flask A, water was added, and the apparatus connected together. The reduced sulphate was then decomposed with dilute hydrochloric acid, the sulphuretted hydrogen given off was absorbed in the arsenic solution in C, C, and D, D, and carbonic acid by the barium and sodium hydrates in E, E, E, E.

The decomposition was completed by boiling the flask A, and finally the flasks B and C, C, are also boiled to expel the carbonic acid that may have been retained in them.

The steam from C, C, raises the tubes D, D, to the boiling point, and all the carbonic acid was thereby expelled and collected in E, E, E, E. The last tube of the series was not found at any time to contain any trace of carbonic acid, thus proving the complete absorption by the previous tubes of the series E.

The contents of the tubes E, E, E, E, were emptied into a beaker, and enough hydrate of baryta added to precipitate all the carbonic acid as carbonate of baryta; this is then filtered off, the filter and its contents placed in a carbonic acid apparatus, and the carbonic acid determined by loss of weight.

The contents of C, C, and D, D, were emptied into a beaker, the filtrate from the carbonate of baryta from E, E, E, E, if it was found to contain any sulphide, was added, and the whole filtered through a tared filter, washed, dried, and weighed.

The contents of flask A were filtered through a tared filter, and the filtrate made up to 500 c.c., of which 100 c.c. were evaporated to dryness for total soda, and 200 c.c. were precipitated with barium chloride for sulphate undecomposed. The platinum crucible, after being thoroughly cleansed, was dried, weighed, ignited, and again weighed, the loss in weight giving sulphur in combination with platinum. The insoluble matter on the filter, washed and dried, is treated with bisulphide of carbon, dried, and weighed; it was then oxidised with nitric acid, filtered, and any metallic platinum estimated. The sulphuric acid thus formed is determined by precipitation with barium chloride in the usual way; the sulphur thus found is calculated into PtS_2; and this amount subtracted from the total weight of residue on the tared filter, gives by difference the amount of unconsumed carbon.

The bisulphide of carbon solution was then evaporated to dryness, and the sulphur weighed.

The first five experiments were made merely as a test as to whether carbonate of soda was formed in the decomposition :—

University of Michigan

A. A mixture of—

Sulphate of soda .... 7·1 grams.
Carbon..... 1·2 „
Equal to $2Na_2SO_4 + 4C$,

submitted to a bright red heat for 45 minutes, yielded for 100 Na_2SO_4 employed—

19·3 per cent. as undecomposed Na_2SO_4.
11·91 „ „ converted into Na_2CO_3.

14·75 per cent. of the Na_2SO_4 decomposed being converted into Na_2CO_3.

B. A mixture of—

Sulphate of soda .... 7·1 grams.
Carbon..... 1·2 „
Equal to $2Na_2SO_4 + 4C$,

submitted to a bright red heat for 60 minutes, yielded for 100 Na_2SO_4 employed—

10·8 per cent. as converted into Na_2CO_3.

C. The crucible was lined with carbon and a mixture of—

Sulphate of soda.... 10·65 grams.
Carbon..... 1·8 „
Equal to $2Na_2SO_4 + 4C$,

was placed in the cavity, and covered with a layer of carbon, the excess carbon amounting to—

3·901 grams.

The crucible was exposed for 45 minutes to a red heat, and then to a high red heat for 15 minutes more.

Yielded for 100 Na_2SO_4 employed—

·50 per cent. as undecomposed Na_2SO_4.
1·00 „ „ converted into Na_2CO_3.

1·05 per cent. of Na_2SO_4 decomposed is converted into Na_2CO_3.

We can here see the effect of the higher temperature and excess of carbon, the amount of Na_2CO_3 being much less than in the cases A and B.

	C.	S.	O.	Na.	Na_2SO_4.
Na_2SO_4 employed	—	22·535	45·07	32·395	100·00
with	53·531	—	—	—	—
Obtained as undecomposed carbon	20·61	—	—	—	—
„ „ Na_2SO_4	—	0·112	0·225	0·162	0·50
„ carbonate Na_2CO_3...	0·084	—	0·335	0·321	1·00
Total obtained	20·694	0·112	0·560	0·483	1·50
As undetermined	—	22·423	—	31·912	98·50
Loss	32·837	—	44·51	—	—

The carbon and oxygen have in this case been given off in such proportions that it is evident the carbon must have been evolved nearly altogether in the form of carbonic oxide.

32·837 carbon require for conversion into CO 43·782 oxygen; whilst 44·51 oxygen has actually been lost. Thus ·738 oxygen apparently has been evolved as CO_2, and of 100 parts carbon employed—

98·34 per cent. has gone to form CO, and
1·66 „ „ „ CO_2.

D. A mixture of—

Sulphate of soda ..... 10·65 grams
Carbon ..... 1·8 „
Equal to $2Na_2SO_4 + 4C$,

submitted to a low red heat over a Bunsen lamp for 30 minutes, then to white heat over a blowpipe for 20 minutes more, yielded for 100 Na_2SO_4 employed—

20·377 per cent. as undecomposed Na_2SO_4
1·340 „ „ converted into Na_2CO_3.

1·68 per cent. of the Na_2SO_4 decomposed being converted into Na_2CO_3.

E. A mixture of—

Sulphate of soda ..... 10·65 grams
Carbon ..... 1·8 „
Equal to $2Na_2SO_4 + 4C$,

submitted to a low red heat over a Bunsen lamp for 60 minutes, yielded for 100 Na_2SO_4 employed—

19·1 per cent. as converted into Na_2CO_3.

A number of subsidiary experiments were made to ascertain the temperature at which the decomposition took place, and it appears from these that below a dull red heat the decomposition of sulphate of soda by carbon does not take place to any appreciable extent, but that at a red heat it takes place readily—

F. A mixture of—

Sulphate of soda ..... 10·65 grams
Carbon ..... 1·8 „
Equal to $2Na_2SO_4 + 4C$

submitted to a dull red heat for 60 minutes over a Bunsen lamp. Approximate temperature 1270° F.

Note.—The temperature in this and succeeding experiments was taken by heating the copper ball of a pyrometer in the same position as the crucible, and taking the temperature thus determined as approximately that of the crucible and contents.

Yielded for 100 Na_2SO_4 employed—

21·73 per cent. as undecomposed Na_2SO_4
23·20 „ converted into Na_2CO_3.

29·64 per cent. of the Na_2SO_4 decomposed being converted into Na_2CO_3.

	C.	S.	O.	Na.	Na_2SO_4.
Employed Na_2SO_4	—	22·535	45·070	32·395	100·00
With	16·901	—	—	—	—
Obtained as undecomposed carbon	—	—	—	—	—
„ „ Na_2SO_4	—	4·897	9·794	7·039	21·73
„ carbonate Na_2CO_3	1·961	—	7·843	7·516	23·20
„ sulphide Na_2S	—	11·412	—	16·400	50·632
„ sulphur, free S	—	3·953	—	—	—
„ „ with Pt = S	—	2·320	—	—	—
Total obtained	1·961	22·582	17·637	30·955	95·562
Undetermined	—	—	—	1·440	4·445
Loss	14·940	—	27·433	—	—

In this experiment the Na not accounted for as undecomposed Na_2SO_4, or as Na_2S and Na_2CO_3, amounted to Na 1·44, and this calculated into Na_2S_2 = 2·004 S = 3·444 Na_2S_2; the total sulphur, free and combined with Pt, amounted to 6·273. Deducting 2·004, we have 4·269 calculated into Na_2S_2 = 10·406 Na_2S = 14·675 Na_2S_2. This added to 3·444 Na_2S_2 = 18·119 Na_2S_2, and as the Na_2S as found = H_2S evolved = 27·812 − 10·406 = 17·406 Na_2S existing as such, there has been decomposed 100 − 21·73 = 78·27 per cent. of the Na_2SO_4 employed, with a loss of oxygen equal to 27·433. As it is shown by experiment C that the excess carbon acts by reducing CO_2 to CO, we must, in calculating the formulæ of the actual decomposition of the Na_2SO_4, take the carbon in the same ratio as the Na_2SO_4, in this case 78·27 per cent.

78·27 per cent. of 16·901 carbon employed = 13·28, corresponding to the equation $2Na_2SO_4 + 4C$. Deducting from this the C equivalent of the Na_2CO_3 = 19·61, there is left 11·267 as evolved in combination with 27·433 oxygen.

Calculating the carbon in the first instance into CO—

$$11·267\ C + 15·022\ O = 26·289\ CO.$$

Then—

$$27·433\ O - 15·022\ O = 12·411\ O.$$

This into CO_2 =

$$12·411\ O + 21·719\ CO = 34·130\ CO_2,$$

and—

$$26·289\ CO - 21·719\ CO = 4·57\ CO.$$

These figures when reduced correspond closely with the formula—

$$10Na_2SO_4 + 20C = 3Na_2CO_3 + 3Na_2S_2 + 4Na_2S + 14CO_2 + 3CO.$$

G. A mixture of—

Sulphate of soda..... 7·10 grams
Carbon ..... 1·20 „
Equal to $2Na_2SO_4 + 4C$,

submitted to a dull red heat for 60 minutes over a Bunsen lamp, approximate temperature 1270° F., yielded for 100 Na_2SO_4 employed—

24·412 per cent. undecomposed Na_2SO_4
26·867 „ converted into Na_2CO_3

35·40 per cent. of the Na_2SO_4 decomposed being converted into Na_2CO_3.

	C.	S.	O.	Na.	Na_2SO_4.
Employed Na_2SO_4.....	—	22·535	45·07	32·395	100·00
With	16·901	—	—	—	—
Obtained as undecomposed carbon	1·109	—	—	—	—
„ „ Na_2SO_4	—	5·440	10·880	7·822	24·142
„ carbonate Na_2CO_3 ..	2·270	—	9·082	8·704	26·867
„ sulphide Na_2S	—	9·124	—	13·116	40·485
„ sulphur, free S.....	—	3·155	—	—	—
„ „ with Pt = S	—	4·746	—	—	—
Total obtained	3·379	22·465	19·962	29·642	91·494
Undetermined.....	—	—	—	—	8·506
Loss	13·522	0·07	25·108	—	—
Total Na determined.....	—	—	—	32·38	—

The Na accounted for by the Na_2CO_3, Na_2S, and undecomposed Na_2SO_4 amounts to 29·642 only, while the amount actually determined is 32·38, the difference 2·738 calculated into Na_2S_2 = 3·809 S = 6·547 Na_2S_2. The total sulphur, free and combined with platinum, is 7·901, this — 3·809 = 4·092 combined with Na_2S to form Na_2S_2 = 9·974 Na_2S = 14·066 Na_2S_2; this added to 6·547 Na_2S_2 = 20·613 Na_2S_2, and as the Na_2S as found from the H_2S evolved = 22·24 — 9·974 = 12·266 as Na_2S.

The loss of carbon amounts to 13·522, and of oxygen to 25·108, while the Na_2SO_4 has been decomposed to the extent of 75·858 per cent. Calculating as in case F on the same proportion of carbon as there has been of Na_2SO_4 decomposed, we have $16·901 \times \frac{75·858}{100}$ = 12·820 — 2·270 (= the carbon as Na_2CO_3) equals 10·550 carbon combined with the 25·108 oxygen. Then—

$10{\cdot}550\ C + 14{\cdot}0660\ O = 24{\cdot}616\ CO,$
$25{\cdot}108\ O - 14{\cdot}066\ O = 11{\cdot}042\ O.$ This into CO_2,
$11{\cdot}042 + 19{\cdot}323\ CO = 30{\cdot}365\ CO_2,$
$24{\cdot}616\ CO - 19{\cdot}323\ CO = 5{\cdot}293\ CO,$

which lead to the approximate formula for the decomposition of—
$11Na_2SO_4 + 22\ C = 4Na_2CO_3 + 4Na_2S_2 + 3Na_2S + 14CO_2 + 4CO.$

H. A mixture of—

Sulphate of soda..... 7·1 grams.
Carbon..... 1·2 „
Equal to $2Na_2SO_4 + 4C$,

submitted to a dull red heat over a Bunsen lamp for 75 minutes, approximate temperature 1260° F., yielded for 100 Na_2SO_4 employed—

24·98 per cent. as undecomposed Na_2SO_4.
25·68 „ „ converted into Na_2CO_3.

34·23 per cent. of the Na_2SO_4 decomposed being converted into Na_2CO_3.

	C.	S.	O.	Na.	Na_2SO_4.
Employed Na_2SO_4.....	—	22·535	45·070	32·395	100·00
With	16·901	—	—	—	—
Obtained as undecomposed C	0·930	—	—	—	—
„ „ Na_2SO_4	—	5·629	11·259	8·092	24·98
„ carbonate Na_2CO_3 ..	2·170	—	8·681	8·319	25·68
„ sulphide Na_2S	—	9·456	—	13·591	41·95
„ sulphur, free S	—	4·183	—	—	—
„ „ with Pt = S	—	3·268	—	—	—
Total obtained	3·100	22·536	19·940	30·002	92·615
Undetermined	—	—	—	—	7·385
Loss	13·801	—	25·130	—	—
Total Na determined.....	—	—	—	32·387	—

The Na not accounted for as undecomposed Na_2SO_4, or as Na_2CO_3, and Na_2S amounted to 2·393, and this calculated into $Na_2S_2 = 3{\cdot}329\ S = 5{\cdot}722\ Na_2S_2$.

The total sulphur, free or combined with platinum, amounted to 7·541; deducting 3·329 as above, we have 4·122; this calculated into $Na_2S_2 = 10{\cdot}047\ Na_2S = 14{\cdot}169\ Na_2S_2$; this added to $5{\cdot}722\ Na_2S_2 = 19{\cdot}891\ Na_2S_2$, and as the Na_2S as found from H_2S evolved = 23·047 − 10·047 = 13·00 Na_2S existing as such.

Then there has been decomposed 100 − 24·98 = 75·020 per cent. of the Na_2SO_4 employed, and calculating the carbon in the same proportion—

$16{\cdot}901 \times \frac{75{\cdot}020}{100} = 12{\cdot}679 - 2{\cdot}17$ (= the carbon as carbonate) = 10·509 carbon combined with 25·130 oxygen.

Then calculating the carbon in the first instance into CO—

$$10{\cdot}509\ C \times 14{\cdot}012\ O = 24{\cdot}521\ CO,$$
$$25{\cdot}130\ O - 14{\cdot}012\ O = 11{\cdot}118\ O.\ \text{This into } CO_2,$$
$$11{\cdot}118\ O + 19{\cdot}456\ CO = 30{\cdot}574\ CO_2,$$
$$24{\cdot}521\ CO - 19{\cdot}456\ CO = 5{\cdot}065\ CO,$$

leading to the approximate formula—

$$3Na_2SO_4 + 6C = Na_2CO_3 + Na_2S_2 + Na_2S + CO + 4CO_2.$$

I. A mixture of—

Sulphate of soda..... 7·1 grams.
Carbon..... 1·2 „
Equal to $2Na_2SO_4 + 4C$,

submitted to a dull red heat over a Bunsen lamp for 60 minutes, approximate temperature 1235° F., yielded for 100 Na_2SO_4 employed—

19·781 per cent. as undecomposed Na_2SO_4.
27·181 „ „ converted into Na_2CO_3.

33·883 per cent. of the Na_2SO_4 decomposed being converted into Na_2CO_3.

	C.	S.	O.	Na.	Na_2SO_4.
Employed Na_2SO_4.....	—	22·535	45·070	32·395	100·00
With	16·901	—	—	—	—
Obtained as undecomposed C	2·211	—	—	—	—
„ „ Na_2SO_4	—	4·458	8·915	6·408	19·781
„ carbonate Na_2CO_3...	2·297	—	9·188	8·805	27·181
„ sulphide Na_2S	—	9·543	—	13·718	42·346
„ sulphur, free S	—	4·070	—	—	—
„ „ with Pt. S ..	—	4·454	—	—	—
Total obtained	4·508	22·525	18·103	28·931	89·308
Undetermined	—	—	—	—	10·692
Loss.....	12·393	—	26·967	—	—
Total Na determined.....	—	—	—	32·45	—

The Na not accounted for as Na_2SO_4 undecomposed, or as Na_2CO_3, and Na_2S amounted to 3·464, and this calculated into $Na_2S_2 = 4{\cdot}819$ S = 8·283 Na_2S_2.

The total sulphur free or combined with platinum amounted to 8·524; deducting 4·819 as above, we have 3·705; this calculated into $Na_2S_2 = 9{\cdot}031$ $Na_2S = 12{\cdot}736$ Na_2S_2; this added to 8·283 Na_2S_2 =

21·019 Na_2S_2, and as the Na_2S as found from H_2S evolved = 23·261 − 9·031 = 14·23 Na_2S existing as such.

Then there has been decomposed 100 − 19·781 = 80·219 per cent. of the Na_2SO_4 employed, and calculating the carbon in the same proportion, $16{\cdot}901 \times \frac{80{\cdot}219}{100} = 13{\cdot}557 - 2{\cdot}297$ (= carbon as Na_2CO_3) = 11·260 carbon combined with 26·967 oxygen.

Then calculating the carbon in the first instance to CO—

11·260 C = 15·013 O = 26·273 CO,
26·967 O − 15·013 O = 11·954 O. This into CO_2,
11·954 O + 20·929 CO = 32·873 CO_2,
26·273 CO − 20·929 CO = 5·354 CO,

leading to the approximate formula—

$$3Na_2SO_4 + 6C = Na_2CO_3 + Na_2S_2 + Na_2S + CO + 4CO_2.$$

Summary of the Experiments.

A and B. These two experiments were merely preliminary, and to prove whether carbonate of soda was or was not formed in the decomposition of sulphate of soda by carbon at a red heat.

C. This experiment shows the effect of excess carbon and higher temperature than red heat, the decomposition giving only a very small proportion of carbonate of soda, and approximating closely to the formula—

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

D. This experiment gave results closely agreeing with C, the carbonate of soda formed being equal only to 1·68 per cent. of the sulphate of soda actually decomposed.

E. This experiment shows that with the proportions used, submitted to a dull red heat, 19 per cent. of the sulphate of soda employed was converted into carbonate of soda.

Note.—A series of subsidiary experiments showed that under a dull red heat little or no decomposition took place.

F. This experiment shows that a mixture of $2Na_2SO_4 + 4C$, submitted to a dull red heat for 60 minutes, has given 29·24 per cent. of the sulphate of soda decomposed, as carbonate of soda, the reaction approximating closely to the formula—

$$10Na_2SO_4 + 20C = 3Na_2CO_3 + 3Na_2S_2 + 4Na_2S + 3CO + 14CO_2,$$

the temperature being about 1270° F.

G. This experiment, with the same mixture as in F, submitted for 60 minutes to about the same degree of heat = 1270° F., gave 35·4 per

cent. of the sulphate of soda decomposed as converted into carbonate of soda, the reaction approximating closely to the formula—

$$11Na_2SO_4 + 22C = 4Na_2CO_3 + 4Na_2S_2 + 3Na_2S + 4CO + 14CO_2.$$

H. This experiment with the same mixture as in F and G, was submitted to a dull red heat for 75 minutes. Temperature about 1260° F. Gave 34·23 per cent. of the sulphate of soda decomposed as converted into carbonate of soda, the reaction approximating closely to the formula—

$$3Na_2SO_4 + 6C = Na_2CO_3 + Na_2S_2 + Na_2S + 4CO_2 + CO.$$

I. This experiment was similar to G, except that the temperature was about 1235° F. It gave 33·883 per cent. of the sulphate of soda decomposed as being converted into carbonate of soda, the reaction approximating closely to the formula—

$$3Na_2SO_4 + 6C = Na_2CO_3 + Na_2S_2 + Na_2S + 4CO_2 + CO.$$

Assembling these formulæ we have—

	F.	G.	H.	I.	Total.	Mean.
Na_2SO_4	10	11	3	3	27	3
C	20	22	6	6	54	6
Na_2CO_3	3	4	1	1	9	1
Na_2S_2	3	4	1	1	9	1
Na_2S	4	3	1	1	9	1
CO	3	4	1	1	9	1
CO_2	14	14	4	4	36	4

These experiments show that:—

1st. When sulphate of soda is mixed with a quantity of carbon in excess of two equivalents, and exposed to a temperature considerably above red heat, out of contact with air, the reaction which takes place is, that the sulphate is ultimately converted into monosulphide of sodium, while the oxygen is evolved as carbon monoxide—

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

2nd. When sulphate of soda and carbon, finely divided and intimately mixed, are exposed to a temperature of dull redness (say from 1150° to 1300° F.), out of contact with the air, there is formed a certain quantity of carbonate of soda, with an equivalent proportion of sodium bisulphide, as well as sodium monosulphide, while the carbon combines with the oxygen of the sulphate of soda to form carbon monoxide and carbon dioxide.

The amount of carbonate and bisulphide formed varies inversely as

the temperature, while the amount of sulphate decomposed varies directly as the temperature.

The reaction which is most in accordance with these experiments being—

$$3Na_2SO_4 + 6C = Na_2CO_3 + Na_2S_2 + Na_2S + 4CO_2 + CO.$$

Any excess of carbon acts apparently in the first instance on the CO_2, reducing it to CO, and finally on the $Na_2CO_3 + Na_2S_2$, producing $Na_2S + CO$.

The decomposition of sulphate of potash by carbon takes place at lower temperature, but as shown by a number of experiments, the decomposition is of the same character as in the case of sulphate of soda, carbonate of potash and bisulphide of potassium being produced.

[Although Liebig was clearly the first to explain the reaction of wood-fibre on Na_2S, such a method of producing alkaline carbonates had been used practically many years previously by soap-boilers, and is thus described in a note book before me dated 1800:—

"*To make Hepar of Soda or Potass from the Sulphates.*

"It is necessary to dry these salts in a reverberatory furnace, then mix them with their weight of fir sawdust, and fuse them in a reverberatory furnace. When the surface becomes calm, the operation is complete—let the sulphure run out. If it is a sulphure of potass, break it up with a hammer, dissolve in water, evaporate it, and when the salt begins to form, put in sawdust till it is thick.

"Then put it into the calcining furnace, roast it for an hour, two-thirds of the sulphate will be decomposed. Separate the undecomposed part by solution.

"If you operate on the sulphate of soda, after the first sulphure is produced, add more sawdust, melt a second time to a sulphure, then operate as with the potass."]

It is not too great an assumption that this is the general type of decomposition for all the alkaline and earthy sulphates, the well known slow decomposition of soluble sulphates by organic matter showing that the formation of bisulphides such as FeS_2 is constantly occurring in the operations of nature.

Even when the materials used in above experiments are moistened with as much as 40 per cent. of water and then heated, the reaction still remains apparently the same, the water no doubt being all driven off before the decomposition of the sulphate by the carbon takes place to any extent.

Having established the formation of Na_2CO_3 and Na_2S_2, it seemed not unlikely that in the usual method of manufacturing alkali by Leblanc's process, that the second atom of sulphur in the Na_2S_2 would be driven off, while the Na_2S then remaining was converted into Na_2CO_3 and CaS, and a series of experiments made to elucidate this point showed most conclusively that no appreciable quantity of sulphur was lost in this way working in closed crucibles. As, however, the Na_2S_2 oxidises very rapidly when exposed to the air while hot, it is probable that a small proportion may be thus lost, when the operation is conducted in large furnaces, where an oxidising flame is employed. I trust to be able shortly to complete an investigation upon this and kindred points in the decomposition of sulphate of soda by carbon and carbonate of lime.

LVIII.—*On the Determination of the Index of Refraction of Liquids by means of the Microscope.*

By H. C. Sorby, F.R.S., President of the Geological Society.

So long ago as the year 1767, the Duke de Chaulnes pointed out how the index of refraction of a transparent parallel plate could be determined by measuring its thickness, and the amount of the displacement of the focal length when an object is viewed through it with a microscope. The method does not, however, appear to have been practically utilised, either in the identification of minerals or in the examination of liquids, and to have become all but lost sight of, until again brought forward by Dr. Royston-Pigott. In the *Monthly Microscopical Journal*, vol. xvi, 1876, p. 294, he described his refractometer for the study of liquids, in which the displacement of the focal length was measured by means of a micrometer screw, placed under the stage of a specially constructed instrument. My aim has been to make such additions to an ordinary microscope that the thickness of the plate and the amount of the displacement of the focal length could be measured with sufficient accuracy, without in any way interfering with the general use of the instrument, especially in the study of minerals. This I have accomplished in two ways, one being most suitable for somewhat thick objects, and the other for those which are thin. I propose in the first case to describe the apparatus, as applied in the case of any transparent substances bounded by parallel planes, and afterwards to explain in some detail its application to such determi-

nations as are likely to be of much interest to the Fellows of the Chemical Society.

Thick Objects.

When the object is somewhat thick, it is far the best to measure its thickness and the displacement of the focus by means of a graduated scale and vernier. A microscope of the Jackson model is admirably suited for this purpose. The silver scale, graduated to $\frac{1}{50}$th of an inch, is attached to the body of the microscope, and a vernier is fixed to the supporting limb. If made and used with care, there is no difficulty in reading off to $\frac{1}{2000}$th of an inch; but since it is difficult to avoid small errors in the graduation, it is best to take more than one series of observations, in different parts of the scale and vernier, which is easily done by altering the position of the object-glass by means of the fine adjustment screw. It is also well to make several measurements at each adjustment, and take the mean of the whole. In this manner very accurate results may be obtained, and the extreme errors can be reduced to probably less than $\frac{1}{2000}$th of an inch.

The thickness of the object is ascertained in the following manner:—Supposing it to be a section of a mineral or other transparent solid, it is fixed down to a supporting glass with Canada balsam, care being taken to squeeze out as much as possible, so that the subjacent layer may be very thin. The glass is then placed on the stage of the microscope, and so arranged that particles of dust on its upper surface, near to the object, are in focus. The exact position on the scale of this focal point is observed, and then the object pushed forwards, so that the position of the focal point for particles of dust or minute scratches on its surface may be similarly determined. Subtracting one from the other, we thus ascertain the true thickness of the object. Several precautions are, however, necessary, in order to avoid small possible errors. In the first place the supporting glass may not be of absolutely uniform thickness. I find that the plate-glass generally used for such a purpose is almost always slightly wedge-shaped, but this is of little consequence if the object is so mounted and placed that the glass may be slidden along the line in which it is equally thick. This is easily ascertained by previous examination with the microscope. The section of the mineral or other object may also itself be unequally thick, and error might arise if the displacement of the focal point were observed in a different place to that of which the thickness was measured. This source of error is, however, readily avoided by having a stop on the stage, up to which the glass is pushed, and the object arranged in the best position by means of the sliding motion of the stage. Another possible source of error is the variation in the focal length of the eye

itself. This may vary very distinctly, according as the focus is adjusted by moving the body of the microscope up or down; in the one case the eye being strained to a short, and the other to a long, focal adjustment. This error may be removed by fixing at the focal length of the upper lens of the eye-piece a small thin glass plate, on which two fine lines are ruled, crossing in the centre. The focus is then so adjusted that particles of dust or small scratches are distinctly visible along with these cross lines. If the instrument is properly constructed and carefully used, I am not aware of any other material source of error. In all cases the very smallest particles of dust should be observed, since there is then the least range in focal adjustment.

Thin Objects.

If the thickness of the object be not too great to be measured by means of the fine adjustment, and especially if it be very thin, it is much better to make use of this method than to employ the graduated scale. In doing so we, however, encounter certain special difficulties. If the milled head of the fine adjustment turns on the screw, and the small arm which moves the lenses rests on a washer, small changes in the points of bearing may give rise to very appreciable differences in what should be uniform readings. In order to overcome this source of error, I have had constructed a fine adjustment, in which the milled graduated head is fixed to the screw, which terminates in a point, working against a small flat steel plate, so as to give an uniform bearing; care has also been taken to ensure the accurate working of the other bearings, and the result is that consecutive measurements, made with moderately high powers, do not differ more than $\frac{1}{20000}$th of an inch. I have not, however, succeeded in so constructing the apparatus that the actual values of the measurements made by the revolution of the graduated head are perfectly uniform for the upper and lower part of the range of movement; but, as explained below, this does not sensibly vitiate the final result.

Displacement of the Focus.

After trying various arrangements, I found that the best object to use to determine the amount of the displacement of the focus caused by looking through a transparent plate is the image of a grating of fine cross lines, ruled on a piece of glass. This is placed as far as the build of the microscope will permit below the lenses of an achromatic condenser, corrected so as to give a sharply defined image through superimposed glass about $\frac{1}{10}$th of an inch thick. When using only a moderate magnifying power, I find that lines ruled $\frac{1}{50}$th of an inch apart give a good result, but with higher powers finer lines $\frac{1}{100}$th of

an inch distant are better. The amount of the displacement is easily observed. If the object is of some size, and perfectly transparent and free from flaws, no great care is needed in arranging it on the stage of the microscope; but, if only certain parts are clear and free from irregularities, it is necessary to move the stage backwards and forwards until a place has been found which shows the lines sharply defined, and not distorted or broken up by irregular refraction or reflection. Having found such a place, the position of the focus is determined, either by the scale or by the graduated head of the fine adjustment, and then the object is pushed sufficiently aside to enable the observer to similarly determine the position of the focus, as seen through the supporting glass alone. The difference between the two sets of measurements gives the amount of displacement due to the transparent plate under examination.

Calculation of the Index.

Having determined in the manner above described the thickness of the parallel plate (T), and the amount of the displacement of the focus (d), the value of the index of refraction (μ) is approximately given by the equation, $\mu = \frac{T}{T-d}$. This has been adopted as strictly true by previous authors, but when I came to measure carefully the index of various minerals and other substances, I found that it invariably gave too high a result, and on fully examining the question I found that, as suggested to me by Professor Stokes, it may be very confidently attributed to the spherical aberration of the object-glass, due to the introduction in front of it of the parallel plate. If the object-glass has been so perfectly corrected that the focal length for the central and marginal rays is the same, I find that the excess in the value of the index is independent of the thickness of the plate, and very closely expressed by the formula, $\frac{1}{4}\left(\mu - \frac{1}{\mu}\right)\sin^2, \frac{\text{aperture}}{2}$. The co-efficient $\frac{1}{4}$ is slightly modified by the special correction of each particular object-glass, and in the case of one of $\frac{2}{3}$ inch focal length, which I have employed, stopped down to an aperture of about 13°, I find that the amounts to be deducted from the calculated index are as shown by the following table:—

Index.	Amount to be deducted.	Index.	Amount. to be deducted.
1·30	·0063	1·70	·0133
1·40	·0082	1·80	·0149
1·50	·0100	1·90	·0165
1·60	·0117	2·00	·0180

These quantities to be deducted from the observed index would not necessarily apply to any other object-glass. If, however, the general kind of correction were the same, and only the aperture different, a similar table for its errors could easily be calculated from one accurate observation. Supposing that the apparent value in the case of a substance having an index of about 1·50 were ·0090 too great, it would merely be requisite to multiply the numbers in the table by ·9, that is to say, by $\frac{\cdot 0090}{\cdot 0100}$.

Magnifying Power used.

In determining the index of objects varying from ·1 to ·4 inch thick, I have found a $\frac{2}{3}$-inch object-glass the most convenient, accompanied by an eye-piece the upper lens of which has a $\frac{1}{2}$-inch focal length. Such a magnifying power answers admirably when we wish to determine the index with great accuracy, and have at disposal an object ·3 or ·4 inch thick. In such a case the measurements are of course made by means of the graduated scale. When only thin objects are at command, I have found that a $\frac{2}{5}$th or $\frac{1}{5}$th object-glass, with the same eye-piece, gives good results, but in this case the measurements are made with the fine adjustment screw. As previously named, the value of the upper and the lower range of movement is not exactly the same, but this source of error may be overcome by measuring the displacement of focus at both the upper and lower range of the screw required to measure the thickness of the object. By a very careful series of observations, I have found that, in the case of my own instrument, the mean of such measurements bears an accurate ratio to the observed thickness, as measured by the entire range, so that the calculated index is sufficiently correct for all practical purposes.

Light employed for Illumination.

In some cases with doubly refracting crystals, if white light be used, the lines of the grating are not sharply defined, but are seen as coloured bands. By employing for illumination the light transmitted by a moderately dark ruby glass, tinted by suboxide of copper, the lines are well defined, even in the above-named special cases. On the whole, I find that bright gas-light transmitted through such red glass is the best illumination, and that the mean index for such light corresponds closely with that for the solar line C. I therefore usually make use of it, and look upon the results as equivalent to the index for that line.

Applications of the Method.

I have already treated at length* on the determination of the indices of minerals, and on the somewhat remarkable phenomena which are seen in the case of uniaxial and biaxial crystals. Since I thought it desirable to describe more particularly the construction and use of the instrument, and am anxious to direct attention to the measurement of the indices of liquids, it appears to me desirable not to enter into the consideration of the special characters of doubly refracting crystals. It may, however, be well to give a few examples in the case of minerals by way of showing how far the measurements of the indices may be relied on. As an illustration, I will refer to a number of observations made with an excellent section of quartz, ·372 inch thick, cut parallel to the axis. The observed index of the ordinary ray was, in different sets of measurements, made as described above, 1·5513, 1·5531, 1·5524, 1·5531, and 1·5513. The mean of these is 1·55224, and, as will be seen, none of the separate observations differ from this by more than a single unit in the third place of decimals, which must be looked upon as a very satisfactory proof of the accuracy with which the measurements may be made. Though one would scarcely expect it in such a mineral as quartz, yet my observations certainly indicate that there is a decided difference in the index for different specimens. The observed values were 1·5522, 1·5582, 1·5478, 1·5552, and 1·5593, the mean of all being 1·5545. In accordance with the principles described above, we must deduct from this ·0108, which leaves 1·5437 as the mean index freed from the errors due to spherical aberration. Rudberg gives as the index for the line C 1·5418, which agrees with my mean result as closely as could be expected, when we consider that it varies in different crystals. It differs only ·0004 from that of my best object.

In a similar manner I found that the index for the ordinary ray of Iceland spar varies slightly in different specimens, but the mean was 1·6537. According to Rudberg, that for the line C is 1·6545. I also found that the index for green fluor was 1·4352, and according to Des Cloizeaux it is 1·434. It will thus be seen that when proper correction is made for the effects of spherical aberration of the object-glass, the errors in the observed indices may be reduced to only one or two units in the third place of decimals, which must, I think, be looked upon as a perfectly satisfactory result.

Correction for thin Glass Covers.

In many cases it is very desirable, or even necessary, to cover the upper surface of an object with thin glass, cemented down with Canada

* Anniversary Address, Mineralogical Society, 1877. Anniversary Address, Royal Microscopical Society, 1878.

balsam. In calculating out the results, due allowance must of course be made for the effects of this cover. The index of the glass commonly used, uncorrected for aberration, is about 1·53. In making our observations, we must determine the position on the scale of minute particles of dust or scratches on the upper surface of the mineral, and also that of particles of dust on the upper surface of the glass. The difference between these is the *apparent* thickness of the cover, along with a small layer of balsam. The real thickness is of course this apparent thickness multiplied by 1·53, that is to say, for every 1·00 of apparent thickness of the cover, the focus of any object seen through it is as it were raised ·53. This applies to both the upper surface of the mineral and to the lines of the grating, so that from the apparent thickness, as measured from the surface of the supporting glass to the scratches, &c., on the top of the specimen, and also from the displacement of the focus, we must deduct an amount equal to the apparent thickness of the covering glass multiplied by ·53.

Determination of the Index of Liquids.

If the liquid be not very volatile, and the amount at command ample, it is on the whole best to use a glass cell made from stout tubing, with an internal bore of a $\frac{1}{4}$ or $\frac{1}{5}$th of an inch. The length may be $\frac{1}{2}$ inch, or somewhat less, according to the focal length of the object-glass employed. This cell must be fixed down to a suitable piece of plate-glass, and when filled with the liquid must be closed at the top with a thin glass cover. If the liquid is water, or an aqueous solution, this cover may be cemented down with a little gold size. In calculating out the results, allowance must of course be made for the effects of the thin glass cover, but if it be sufficiently large to project somewhat beyond the outside of the cell, the focal point of the grating may be observed through it in such a manner that the value of d is true without need of any such correction. If the cell could be cut so that the opposite faces were absolutely parallel, the real thickness of the liquid might be determined by measuring the distance between the supporting glass and the thin cover; but, since we cannot rely on the result to $\frac{1}{2000}$th of an inch, it is better to measure the thickness of the cover, and make the necessary allowance in the manner described above, or else to adopt another method.

In no case is it desirable to trust to the depth of the cell itself, since the thickness of the film of liquid between it and the cover may vary. We may, however, measure the apparent thickness (t) of the liquid from the upper surface of the supporting glass to the under side of the cover, which, of course, is equal to the real thickness (T), less the

displacement of focus (d). The formula for the index of refraction, $\frac{T}{T-d}$, then becomes $\frac{t+d}{t}$.

If the amount of liquid at disposal is only small, it is not desirable to use a cell, but we may very conveniently employ a so-called *live box*. This has also the advantage that it enables us to determine the index of very volatile liquids without any difficulty. The apparatus to which I refer has a bottom glass raised up in a short tube, over which slides a cap holding the thin glass cover. A small drop of the liquid may be placed in the centre of the lower glass, and the upper glass brought down until it touches the liquid, and, if necessary, somewhat drawn back again, or so arranged that the space between the glasses incloses a suitable thickness of liquid. It is then easy to measure the true distance between the glasses close to the included drop, and the displacement of the focus due to it. We thus obtain at once the true values of T and d, independent of the effect of the thin glass cover. Being so completely inclosed, volatile liquids evaporate very slowly, and, if they do, the only effect is to reduce the width of the drop, without in any way changing the thickness.

As an example, I may give the results obtained in the case of water, using a cell nearly $\frac{1}{2}$ inch in depth. Corrected for the effects of spherical aberration, I found that the index was 1·329. That for the line C given in Watts' *Dictionary of Chemistry* is 1·330, which shows that with a cell $\frac{1}{2}$ an inch deep, and measuring with the graduated scale, very accurate results may be obtained. By using the fine adjustment fixed to my microscope, an equally accurate determination might be made with $\frac{1}{10000}$th part of a cubic inch of a liquid inclosed between the glasses of a live box. In order to insure so small an error as only one or two units in the third place of decimals, great care is required; but, if it were unnecessary to determine the index true beyond the second place, the method I have described will be found very convenient, when only small quantities of liquids are at disposal. This fact, coupled with the great simplicity of the measurements, is, I think, a strong recommendation to the method here described.

LIX.—*On the Action of Sodium on the Benzyl Ether of Isobutyric Acid.*

By W. R. Hodgkinson, Ph.D.

I showed, in 1877 (*Berlin Berichte*, x, 65), in conjunction with Max Conrad, that the action of sodium on the benzyl ether of acetic acid is not analogous to that which it has on the acetic ethers of the lower numbers of the $C_nH_{2n+1}OH$ series of alcohols. Whilst the latter form according to one or other of the following equations, the C_nH_{2n+1} (or alkyl) ether of sodium acetoacetic acid and sodium ethylate:—

$$\text{I. } 2\,\begin{matrix}CH_3\\|\\CO.OC_2H_5\end{matrix} + Na_2 = \begin{matrix}CO.CH_3\\|\\CHNa.CO.OC_2H_5\end{matrix} + H_2 + NaO.C_2H_5.$$

$$\text{II. } 3\,\begin{matrix}CH_3\\|\\CO.OC_2H_5\end{matrix} + 2Na_2 = \begin{matrix}CO.CH_3\\|\\CHNa\\|\\CO.OC_2H_5.\end{matrix} + 3NaO.C_2H_5.$$

the primary products of the action of sodium on benzyl acetate are sodium acetate and the benzyl ether of hydrocinnamic acid (hydrocinnameïn):—

$$\text{III. } 4\,\begin{matrix}CH_3\\|\\CO.OCH_2.C_6H_5\end{matrix} + Na_2 = 2\,\begin{matrix}CH_3\\|\\COONa\end{matrix} + 2\,\begin{matrix}CH_2.CH_2.C_6H_5\\|\\CO.OCH_2.C_6H_5\end{matrix} + H_2.$$

and, secondarily, hydrocinnamic and cinnamic acids as sodium salts and toluene:—

$$\text{IV. } 2\,\underset{\text{Hydrocinnameïn.}}{\begin{matrix}CH_2.CH_2.C_6H_5\\|\\CO.OCH_2.C_6H_5\end{matrix}} + Na_2 = \underset{\text{Sodium phenyl-propionate.}}{\begin{matrix}CH_2.CH_2.C_6H_5\\|\\CO.ONa\end{matrix}} + \underset{\text{Sodium phenyl-acrylate.}}{\begin{matrix}CH{=}CH.C_6H_5\\|\\CO.ONa\end{matrix}} + 2C_6H_5.CH_3.$$

$$\text{V. } 2\,\begin{matrix}CH_2.CH_2.C_6H_5\\|\\CO.OCH_2.C_6H_5\end{matrix} + Na_2 = 2\,\begin{matrix}CH{=}CH.C_6H_5\\|\\CO.ONa\end{matrix} + H_2 + 2C_7H_8.$$

In an extension of our work we found that the ethers of propionic and normal butyric acids behave in quite an analogous manner: the ether of the latter acid giving, according to reaction III, the benzyl ether of α-benzyl-butyric acid or benzyl-ethyl hydrocinnamate:—

$$\begin{array}{l} CH_2.CH_3 \\ | \\ CH.CH_2.C_6H_5 \\ | \\ CO.OCH_2C_6H_5 \end{array}$$

which also, following equations IV and V, further yield the sodium salts of ethyl hydrocinnamic and ethyl-cinnamic acids and toluene.

Although the benzyl ethers of the normal fatty acids, or more generally of the ($C_nH_{2n+1}.CH_2.COOH$) series of acids, comport themselves similarly towards sodium, the same, for want of experimental evidence, could not be said of ethers of acids containing $2(C_nH_{2n+1})$.

In the case of isobutyric acid, the action could only be predicted to proceed so far as the formation of a benzylated acid, according to the reasoning of equation III :—

$$\text{VI. } 4\left|\begin{array}{l} CH(CH_3)_2 \\ CO.OCH_2.C_6H_5 \end{array}\right. + Na_2 = 2\left|\begin{array}{l} C(CH_3)_2.CH_2.C_6H_5 \\ CO.OCH_2.C_6H_5 \end{array}\right. + 2\left|\begin{array}{l} CH(CH_3)_2 \\ COONa \end{array}\right. + H_2.$$

This benzyl-dimethacetic acid could evidently not be further affected after the manner of equations IV and V.

I have therefore studied, to some extent, the action of sodium on benzyl isobutyrate.

Benzyl Isobutyrate, $CH.(CH_3)_2CO.OCH_2.C_6H_5$.

This substance was prepared similarly to the benzyl ethers of the normal fatty acids by heating potassic isobutyrate with an equivalent quantity of $C_6H_5.CH_2Cl$, dissolved in alcohol, for four or five days, in a retort attached to a condenser ; the mass was then treated with water, and the oil which separated fractionally distilled. The oil came over completely between 225° and 230°, and a second distillation yielded the pure substance boiling at 228° (normal thermometer entirely in vapour). Two combustions gave the following results :—

I. ·1475 gram = ·1030 OH_2, and ·3960 CO_2.
II. ·0995 „ = ·0712 „ and ·2690 „

			I.	II.
C_{11}	132	74·16	73·22	73·73
H_{14}	14	7·86	7·76	7·95
O_2	32	17·98	—	—
	178	100·00		

It is a powerfully refracting liquid, of sp. gr. 1·0160 at 22° compared with water at 17·5°, and has a very pleasant odour.

Action of Sodium on Benzyl Isobutyrate.

90 grams of the ether were treated with 8 grams of finely cut sodium in a retort with condenser. Scarcely any action took place at the ordinary temperature, but on warming, towards the melting point of sodium, a violent action with evolution of hydrogen set in, the sodium being almost entirely dissolved without further external heating. On adding water to the cooled product—a solid yellowish mass—an oil rose to the surface, a sodium salt being dissolved.

(1.) The oil began to boil about 120°, but the temperature rose quickly to 250°, between which and 300° the whole passed over. By repeated distillation of the fraction 120—200°, a mobile liquid, smelling like toluene and boiling at 110—112°, was finally obtained; this gave the following figures on analysis:—

I. ·1658 gram substance = ·1347 OH_2 and ·5491 CO_2.
II. ·1727 gram (again distilled) = ·1310 OH_2 and ·5785 CO_2.

			I.	II.
C_7	84	91·30	90·32	91·36
H_8	8	8·70	9·03	8·43
	92	100·00		

The fraction 250—300° came over on distillation mostly between 290° and 300°, leaving each time a small residue of still higher boiling point.

As it was possible that this high-boiling substance might be the result of decomposition at each distillation, I made combustions of different preparations of the 290—300° fraction with the annexed results:—

(I.) ·1420 gram = ·0985 OH_2 and ·4253 CO_2.
(II.) ·1242 „ = ·0900 „ and ·3769 „
(III.) ·1701 „ = ·1230 „ and ·5145 „

	(I.)	(II.)	(III.)
C	81·68	82·76	82·49
H	7·71	8·05	8·05
O	10·61	9·19	9·48

These values of the three elements not only do not agree with that of the sought-for ether, $C_{18}H_{20}O_2$, but also do not agree amongst themselves: the first of the above figures leading to the improbable formula $C_{20}H_{22}O_2$, the two latter giving the formula $C_{23}H_{26}O_2$.

	($C_{18}H_{20}O_2$.)	($C_{20}H_{22}O_2$.)	($C_{23}H_{26}O_2$.)
C	80·60	81·64	82·64
H	7·46	7·48	7·78
O	11·94	10·88	9·58
	100·00	100·00	100·00

To prevent decomposition by possible over-heating, fresh portions of the fraction 250—300° were repeatedly distilled under a pressure of 40 mm., whereby the greater portion was easily obtained boiling between 200—210°, and a smaller residue at about 280°.

The fraction 200—210° boils under the ordinary pressure at 280° to 285°, and is a somewhat mobile, colourless, highly refractive liquid of pleasant aromatic odour.

The numbers obtained on analysis agree with the formula of benzyl-dimethyl-benzyl acetate :—

I. ·1428 gram = ·1006 OH_2 and ·4200 CO_2.

II. ·1084 „ = ·0765 „ and ·3180 „

Refractioned at 285° (normal thermometer in vapour).

III. ·1530 gram = ·4530 CO_2, water lost.

	$C_{18}H_{20}O_2$.	I.	II.	III.
C	80·60	80·21	80·01	80·75
H	7·46	7·82	7·84	—
O	11·94	—	—	—
	100·00			

Its sp. gr. at 18° = 1·0285 compared with water at 17·5°.

The portion boiling at 280° under a pressure of 40 mm. distilled under ordinary pressure at 340° to 350° without decomposition, and on combustion gave the following results :—

·1031 gram substance = ·0736 OH_2 and ·3180 CO_2,

approximating to the formula $C_{14}H_{16}O$.

	Calculated.	Found.
C_{14}	84·00	84·12
H_{16}	8·00	7·93
O	8·00	—
	100·00	

This substance, which may be regarded as the principal product of the action of sodium on benzyl-dimethyl-benzyl acetate, will be again referred to later on.

(2.) The watery solution of the product of the reaction of sodium on benzyl isobutyrate was strongly acidified with sulphuric acid and extracted with ether, which on evaporation left a residue of oily organic acids of strong isobutyric odour separable by distillation into a portion boiling between 152—157°, and remaining liquid on cooling, and a portion between 240° and 250° solidifying in the neck of the retort.

The fraction 152—157° gave numbers agreeing with those required by isobutyric acid :—

·2365 gram substance = ·1925 OH_2 and ·4717 CO_2.

	Calculated.	Found.
C_4	54·55	54·40
H_8	9·00	9·04
O_2	36·35	—
	100·00	

The silver salt gave:—

·1680 gram substance = ·0535 OH_2, ·1482 CO_2 and ·0925 Ag.

C_4	24·62	24·06
H_7	3·59	3·54
Ag	55·38	55·06
O_2	16·41	—
	100·00	

The portion boiling at 240° to 250°, and solidifying on cooling, was to all appearance benzoic acid. On distillation with steam and recrystallisation it melted at 119—120°; the analysis gave—

I. ·1700 gram = ·0675 OH_2 and ·4268 CO_2.

II. ·0950 „ = ·0445 „ and ·2395 „

		I.	II.
C_7	68·85	68·47	68·76
H_6	4·92	4·41	5·20
O_2	26·23	—	—
	100·00		

The products of the action of sodium on benzyl isobutyrate are, therefore, hydrogen, benzyl benzyl-dimethacetate, sodic isobutyrate and benzoate, toluene, and the oil $(C_{14}H_{16}O)_n$, the production of the first three of which is expressed in equation VI, sodic benzoate, toluene, and the oil, $(C_{14}H_{16}O)_n$, being probably the result of secondary action.

Action of Sodium on Benzyl Benzyl-dimethacetate.

To test the correctness of the above statement of the reaction, pure benzyl benzyl-dimethacetate was treated with sodium, the liquid being heated to the melting point of the latter to induce reaction, which then took place without further heating. The same solid product was treated with water as before. From the oily layer a small quantity was separated by fractional distillation, boiling between 110—112°, and identified as toluene.

On distillation of the higher-boiling portion under a pressure of 40 mm., with the exception of a little unaltered ether boiling at 200—210°, all came over as a thick oil at about 280°, and this latter portion

distilled completely and without the least decomposition under ordinary pressure at 350—355°. On combustion it gave the following numbers:—

I. ·1260 gram gave ·0929 OH_2 and ·3890 CO_2.
II. ·0865 „ ·0625 „ and ·2665 „

These results proclaim the identity of this product and the one obtained in small quantity by the action of sodium on benzyl dimethacetate for the formula $C_{14}H_{16}O$ requires—

		I.	II.
C	84·00	84·20	84·03
H	8·00	8·19	8·03
O	8·00	—	—
	100·00		

The watery solution, treated with sulphuric acid and extracted with ether, furnished an oily mass from which crystals of benzoic acid separated on cooling. From the liquid portion a small quantity was obtained boiling below 200°, and by its physical properties was identified with isobutyric acid.

The solid part, after distillation with steam and crystallisation, melted at 119—120°, and gave the numbers required by benzoic acid.

·2050 gram = ·0970 OH_2 and ·5133 CO_2
= H 5·26 per cent., C 68·29 per cent.; theory requires
H 4·92 per cent., C 68·85 per cent.

(1.) *Saponification of Benzyl Benzyl-dimethacetate.*

This ether is very slowly attacked by aqueous or alcoholic solutions of alkaline hydrates, and does not yield benzyl-dimethacetic acid as might have been expected. From 30 grams of ether boiled with a hot concentrated solution of baric hydrate for 14 days, only 1·5 gram of a mixture of barium salts, soluble in alcohol, was obtained.

On addition of hydrochloric acid an acid oil was precipitated which partly solidified; the solid pressed from the liquid portion, and distilled with steam, gave crystals melting finally at 119—120°, yielding on analysis:—

·0957 gram substance = ·0418 OH_2 and ·2410 CO_2
= H 41·85 per cent., C 68·68 per cent.; theory for benzoic acid,
H 41·92 per cent., C 68·85 per cent.

The watery solution acidulated with hydrochloric acid, was exhausted with ether, and the portion of oil extracted boiling between 150—158°, soluble in water, made into silver salt.

·0640 gram substance = ·0213 OH_2, ·0585 CO_2, and ·0350 Ag.

		Found.
C_4	24·62	24·93
H_7	3·59	3·70
Ag	55·38	54·69
O_2	16·41	—
	100·00	

Benzyl alcohol if formed during the saponification could not be separated from the comparatively very large volume of unchanged ether.

Concentrated alcoholic potash boiled with the ether for nearly three weeks failed to saponify so much as the baric hydrate.

A further proof of the non-production of benzyl-dimethacetic acid was afforded by the behaviour of the ether on heating with soda-lime in a distillation flask. In the first experiment the temperature was raised to about 200°, when a somewhat considerable quantity of thin oily distillate was obtained, smelling strongly of toluene, and coming over on first fractionation at 105—115°.

I. ·0797 gram = ·0650 OH_2 and ·2593 CO_2.
II. ·0780 gram lost ·2585 CO_2.
Refractioned 109—110° gave
III. ·1245 gram = ·1010 OH_2 and ·4176 CO_2.

	C_7H_8.	I.	II.	III.
C	91·30	88·73	90·38	91·48
H	8·70	9·06	—	9·01

The residue in the flask washed out with water, decomposed with hydrochloric acid and extracted with ether, gave on evaporation of the latter a mixture of oily acids partly solidifying on cooling. Fractionation yielded much between 150—160°, further identified as isobutyric acid. Its watery solution was made into calcium salt, which on concentration and heating to 70° did not precipitate. On crystallisation it formed shining prisms of $(C_4H_7O_2)_2Ca + 5OH_2$, as the analysis shows:—

I. ·5705 gram, air dried, lost at 100° ·1760 OH_2.
II. ·3203 „ „ „ ·0985 OH_2.

	Per cent.	I. Per cent.	II. Per cent.
Calculated, OH_2	29·61	30·85	30·75

III. ·4075 gram dry salt, strongly ignited, gave ·1077 CaO.
Theory = CaO 26·17 per cent. III. = 26·43 per cent.

The fraction above 200°, solidifying on cooling, melted after purifica-

tion in the usual manner at 120°, and showed itself to be quite pure benzoic acid:—

I. ·0957 gram substance gave ·0418 OH_2 and ·2410 CO_2.
II. ·1592 gram (fused) gave ·0722 OH_2 and ·4010 CO_2.

		I.	II.
C_7	68·85	68·68	68·70
H_6	4·92	4·85	5·04
O_2	26·23	—	—
	100·00		

Its barium salt dried at 100° yielded—

I. ·1974 gram = ·1018 $BaCO_3$.
II. ·1250 gram = ·0640 $BaCO_3$.

$(C_7H_5O_2)_2Ba$ = Ba 36·15 per cent. I = 35·86 per cent.
II = 35·61 per cent.

As other products than those described could not be found, the action of alkalis on benzyl-benzyl-dimethacetate may perhaps be represented thus:—

$$\text{VIII.}\quad \begin{matrix} C(CH_3)_2.CH_2.C_6H_5 \\ | \\ CO.OCH_2.C_6H_5 \end{matrix} + 2NaOH = \begin{matrix} CH(CH_3)_2 \\ | \\ COONa \end{matrix} + CH_3.C_6H_5 + C_6H_5.COONa + H_2.$$

The conversion of benzyl compounds by alkalis into salts of benzoic acid and toluene was observed by Cannizzaro (*Annalen*, xc, 252), and it is only here remarkable that in the saponification the benzyl-group directly combined with the carbon of the acid radicle, as well as the ether-forming benzyl-group, should be split off, an oxidation to benzoic acid and reduction to toluene simultaneously taking place.

To get at some idea of the structure of the oil $C_{14}H_{16}O$, I attempted its oxidation with chromic acid, but after about ten days' heating, the amount of benzoic acid produced was so small that it only sufficed for qualitative recognition. Soda-lime at 200° had very little more effect, whilst baric hydrate solution and alcoholic potash have no action.

As the simple production of benzoic acid does not throw any light on the constitution of the oil $C_{14}H_{16}O$, an equation fully expressing the action of sodium on benzyl-benzyl-dimethacetate, in which, together with hydrogen, toluene, sodic benzoate, and isobutyrate, it is the principal product, cannot as yet be formed.

Conclusions from the above results.

(1.) Benzyl isobutyrate is exactly analogous in its behaviour with sodium to the benzyl ethers of acetic, propionic, and normal butyric acids:—

$$4\left|\begin{matrix}CH_2.CH_2.CH_3\\ CO.OCH_2C_6H_5\end{matrix}\right. + Na_2 = 2\left|\begin{matrix}CH_2.C_2H_5\\ CO.ONa\end{matrix}\right. + 2\left|\begin{matrix}CH(C_2H_5)_2.CH_2.C_6H_5\\ CO.OCH_2.C_6H_5\end{matrix}\right. + H_2.$$

$$4\left|\begin{matrix}CH(CH_3)_2\\ CO.OCH_2C_6H_5\end{matrix}\right. + Na_2 = 2\left|\begin{matrix}CH(CH_3)_2\\ COONa\end{matrix}\right. + \left|\begin{matrix}C(CH_3)_2CH_2C_6H_5\\ CO.OCH_2.C_6H_5\end{matrix}\right. + H_2.$$

The replaceability of hydrogen at the carbon atom immediately in combination with carboxyl by the benzyl-group under the influence of sodium is probably general with all acids having such hydrogen combinations.

(2.) The benzylated benzylic isobutyrate does not, however, comport itself towards sodium like the before-mentioned ethers of the fatty normal series. In the latter case there is formed, together with toluene and salts of benzylated fatty acids, acids of the cinnamic series with two atoms less hydrogen. But with the iso-body, $C_{18}H_{20}O_2$, such an action evidently cannot take place, the carbon directly connected with carboxyl having no hydrogen atom.

(3.) In the saponification of ethers of normal benzylated fatty acids the benzyl-group of the acid radicle is not affected by alkalis, benzylated fatty acids being produced.

$$\left|\begin{matrix}CH_2.CH_2.C_6H_5\\ CO.OCH_2.C_6H_5\end{matrix}\right. + \alpha.OKH = \left|\begin{matrix}CH_2.CH_2.C_6H_5\\ CO.OK\end{matrix}\right. + (\alpha-1)HOK + HO.CH_2.C_6H_5.$$

In the isobutyric group, however, the benzyl-group is evidently not so firmly combined, since alkalis reproduce isobutyric acid by saponification, the acid as well as the ether benzyl-group being liberated.

Whether the saponification reaction takes place according to a previous equation, or after this one,

$$3\left|\begin{matrix}C(CH_3)_2C_6H_5\\ CO.O.CH_2C_6H_5\end{matrix}\right. + 5NaOH = 3\left|\begin{matrix}CH(CH_3)_2\\ COONa\end{matrix}\right. + \begin{matrix}2(C_6H_5.COONa)\\ 4C_6H_5.CH_3\end{matrix} + OH_2,$$

I do not at present venture to decide.

This research was carried on in the University Laboratory, Würzburg, under the direction of Prof. Wislicenus, to whom I am much indebted for kind assistance and advice.

LX.—*Second Report to the Chemical Society on "Researches on Some Points in Chemical Dynamics."*

By C. R. Alder Wright, D.Sc. (Lond.), Lecturer on Chemistry, and A. P. Luff, Demonstrator of Chemistry, in St. Mary's Hospital Medical School.

In the first report it was shown that when oxide of copper and ferric oxide are reduced by the three agents, carbon oxide, hydrogen, and amorphous carbon, the temperatures at which reduction first becomes perceptible, after a time varying from a few minutes to half an hour or so, depend firstly on the physical condition of the metallic oxide employed and, in the case of carbon, on that of the carbon; and secondly on the amount and character of the heat disturbance ensuing during the reaction, the rule being uniformly noticeable in comparable cases that the greater, algebraically speaking, is the heat evolution (*i.e.*, the greater the actual evolution if the heat disturbance be of + sign, and the less the heat absorption if the heat disturbance be of − sign), the lower is the temperature of initial action. Moreover, it has been shown that the temperatures at which these three agents first begin to act on cuprous oxide are no further removed from those at which they begin to act on various forms of cupric oxide than may be reasonably supposed to be due to difference in physical state; this being a particular case of the above rule, since the heats of combustion of copper to Cu_2O and to CuO are practically the same (calculated per equal amounts of oxygen consumed).

In order to see if these rules are also obeyed by other metallic oxides, experiments have been made, as described below, with different kinds of oxides of various other metals; the determinations were made in the main in the same way as those described in the first report, the chief differences being that, in determining the temperatures of initial action of carbon oxide, the paraffin bath was mostly discarded, the air-bath arrangement described in the first report as employed in certain cases for temperatures above 250°, being used instead, as more convenient; and that in some cases the criteria adopted as to the temperatures at which action commenced were, for reasons dependent on the nature of the oxides examined, different from those employed in the case of the oxides of copper and iron; thus in many cases, especially with hydrogen, the temperature of initial action was determined by finding at what temperature a perceptible loss of weight first took place after 15 minutes or more exposure to the reducing agent; in some instances (with super oxides) the loss of oxygen was arrived at

by boiling the substance with hydrochloric acid, receiving the evolved chlorine in potassium iodide solution, and titrating the iodine liberated; by comparing the numbers thus found before exposure and after, the amount of oxygen removed was readily deducible (this method is referred to briefly, hereafter, as the "iodine process"). In some instances samples of amorphous carbon, prepared from carbon oxide by ferric oxide, but different from the specimen used in the first report, were employed, wherefore the corrections for amount of occluded gases are not always the same; and in a few cases a bath of sulphur vapour was employed instead of a melted solder bath with test pieces of metal when a temperature of about 420° was required.

§ 1. Oxides of Iron Lower than Ferric Oxide.

(A.) *Ferrous Oxide.*

It has been shown by Lowthian Bell (*Chemical Phenomena of Iron Smelting*, p. 28), that when a mixture of equal volumes of carbon oxide and dioxide is passed over ferric oxide at a red heat, reduction goes on until about one-third of the oxygen in the ferric oxide is removed; whilst, conversely, spongy metallic iron heated in the same gaseous mixture to the same temperature, becomes oxidised to an extent indicating an addition of about two-thirds of the quantity of oxygen requisite to form ferric oxide; in other words, that whether metallic iron or ferric oxide be originally employed, the resultant substance is an oxide of composition tolerably close to that indicated by FeO.

A quantity of this stable oxide was prepared by passing equal volumes of carbon oxide and dioxide (prepared from oxalic acid and sulphuric acid) over pure ferric oxide at a bright red heat, for eight hours. After cooling down in a stream of the mixed gases, 1·3680 gram of the product gave 1·4870 Fe_2O_3, whence the composition was nearly that indicated by FeO; in order to make sure that the action had gone on as far as possible the whole was well intermixed, and heated again to a bright red heat in the same gaseous mixture for eight hours more. After cooling, 1·0425 gram gave 1·1360 Fe_2O_3,

	Calculated.		Found.	
	For Fe_2O_3.	For FeO.	After 1st 8 hours.	After 2nd 8 hours.
Fe =	70·00	77·78	76·09	76·28

whence scarcely any change had been produced during the second eight hours. The substance finally obtained contained a perceptible amount of occluded gases; on heating in a Sprengel vacuum it be-

haved in just the same way as carbon, *i.e.*, on heating to a given temperature gas was given off for a few minutes, and the evolution then ceased; on raising the temperature to another limit, more gas came off for a short time, and then entirely ceased coming off; whilst on further raising the temperature the same result again occurred. The following amount of gas was extracted per gram of substance:—

At 360° (in mercury vapour).....	1·83	c.c. at 0°	and 760 mm.
360—420° (up to melting point of zinc)	1·50	„	„
420—460° (antimony thoroughly melted)	0·67	„	„
	4·00		

Of this gaseous mixture, 12·5 per cent. was absorbed by potash, the remainder being almost wholly carbon oxide; whence it results that the composition by weight of the ultimate product was—

Iron.....	76·28
Occluded CO + CO_2....	0·53
Oxygen (by difference)..	23·19
	100·00

Or, omitting the occluded gases, the composition approximated to FeO, being much more nearly $Fe_{16}O_{17} = 14FeO,Fe_2O_3 = 13FeO,Fe_3O_4$.

	Calculated.		Found.
	For FeO.	For $Fe_{16}O_{17}$.	
Iron	77·78	76·71	76·68
Oxygen.....	22·22	23·29	23·32
	100·00	100·00	100·00

No iron in the metallic form was present, as on digesting with boiled water and iodine, no trace of iron was dissolved out.

The action of carbon oxide on this substance, when examined as described in the first report, was found to be imperceptible at all temperatures below 270°; at 275° the baryta-water just began to grow turbid after 3—4 minutes' passage of gas, and at 290° it became very turbid after the passage of only a few bubbles of gas.

In order to find out how far determinations by loss of weight would agree with those made with baryta-water as a test of initial action, 0·794 gram was heated in a narrow **U**-tube containing the oxide at the bend, with a plug of glass wool in front of the oxide, to prevent any

mechanical loss of particles by the current of carbon oxide, which was passed through the tube heated by an air-bath. No appreciable loss of weight was observed below and up to 270°; at 280° the loss after 15 minutes was 0·0025 = 0·31 per cent. Hence both the baryta-test and the loss of weight experiment indicated about 275° as the temperature of initial action; but as gases containing CO_2 were expelled at this temperature on heating in a Sprengel vacuum, it is possible that the turbidity of the baryta-water and the loss of weight were partly due to this cause, although not wholly, inasmuch as the gas expelled on heating to 360° in a Sprengel vacuum, corresponded to only 0·24 per cent. by weight, and hence the amount expelled at 280° would have been less than this, and consequently less than the 0·31 per cent. lost on heating in carbon oxide for 15 minutes. To settle this point definitely the experiment was repeated, a current of pure nitrogen (from ammonium chloride and potassium nitrite) being substituted for carbon oxide. After passing through baryta-water for 15 minutes, the effluent gas produced a trace of turbidity in baryta-water, the substance being heated to 290—300°; the amount of occluded gas expelled, however, was so minute that no perceptible loss of weight was produced in 1·4330 gram of substance, the loss being less than 0·25 milligram, and hence less than 0·02 per cent. The same result was found on heating to 320° in a current of nitrogen for 15 minutes; no appreciable loss of weight occurred either in this case or in another experiment in which air was substituted for nitrogen, the temperature being kept at 300° or 15 minutes.

It hence results, firstly, that about 275° is the true temperature of initial action of CO on the ferrous oxide used; and secondly, that the gas occluded by the ferrous oxide is removed far more rapidly by heating *in vacuo* for a short time than in air or nitrogen; *i.e.*, gases do not under all circumstances act as vacua to one another.

The temperature of initial action of hydrogen was determined by the loss of weight process; the weighings were always made with the tube full of hydrogen, the exit end being first closed by a tightly fitting india-rubber cap, and the entrance end being then disconnected from the hydrogen generator and rapidly closed in the same way; it was found that with due care entrance of air could always be avoided, so that no error was introduced by the displacement of hydrogen by the heavier air. In this way no loss of weight was noticeable after 15 minutes' action at various temperatures below 300°, or at that temperature.

At 310° 0·9200 gram lost in 15 minutes 0·0010 gram = 0·11 per cent.

At 360° (boiling mercury) 0·7460 lost in 15 minutes 0·0100 gram = 1·34 per cent.

At 360° (boiling mercury) 0·7460 lost in 30 minutes 0·0160 gram = 2·14 per cent

A visible condensation of moisture was observed in the last two experiments; that the small loss of weight in the first experiment was not due to the removal of occluded gases, is evident from the circumstance above mentioned, that on heating in a current of nitrogen for 15 minutes at 320° no appreciable loss of weight occurred.

Hence 305° may be taken as the temperature of initial action of hydrogen on this ferrous oxide.

In order to determine the temperature of initial action of carbon, 0·6 gram of the oxide and 0·3 of carbon (from CO) were ground together in an agate mortar and treated as described in the first report. The following numbers were obtained, the amounts of gas collected being given in c.c. at 0° and 760 mm.:—

Range of temperature	Up to 360°	360—440°	440—460°
Time of heating in minutes..	30	15	15
Carbon dioxide collected	0·6	—	1·5
Other gases	1·2	—	2·8
Total gas collected	1·8	2·5	4·3
Gas occluded by ferrous oxide	1·1	2·0	2·0
Ditto by carbon.....	0·3	0·4	0·4
Total gas due to occlusion ...	— 1·4	— 2·4	— 3·2
Gas due to reduction of FeO.	0·4	0·1	1·1

Up to 440° the expulsion of gas was fitful, going on for a short time on raising the temperature, and then stopping till the temperature was again raised; in short, the gas collected was simply that due to occlusion. At 450° and upwards, however, a slow regular evolution of gas was observed, whence the temperature of initial action may be taken as being 450°.

It results from these experiments that the temperatures of initial action of carbon oxide, hydrogen, and carbon are situated respectively at near 275°, 305°, and 450°, following the same order as that observed with ferric oxide and the oxides of copper.

(B.) *Ferroso-ferric Oxide.*

Magnetic oxide of iron was prepared from the rolling mill scales of boiler plate manufacture by finely powdering, sifting, and digesting

with a solution of iodine in potassium iodide to dissolve out particles of metallic iron; about 0·3 per cent. of metal was thus extracted; the whole was then quickly filtered and washed successively with water, alcohol, and ether, and exposed to the air. The oxide thus obtained gave the following numbers on analysis, 1·55 per cent. of SiO_2 being subtracted; the ferrous iron was determined by titration with permanganate:—

	Calculated for Fe_3O_4.		Found.
Fe as FeO	24·14		24·17
Fe as Fe_2O_3	48·28		48·76
O.....	27·58	(by diff.)	27·07
	100·00		100·00

On heating to redness in a Sprengel vacuum, no gas was given off.

The action of carbon oxide was found to begin at 200° by the baryta-water test, CO_2 being copiously formed at 215°.

Hydrogen caused no loss of weight at temperatures below and up to 280°.

At 300° 1·3640 gram lost in 15 minutes 0·0010 gram = 0·07 per cent.

At 360° (mercury vapour) 1·163 gram lost in 15 minutes 0·0050 gram = 0·43 per cent.

At 360° (mercury vapour) 1·163 gram lost in 30 minutes 0·0150 gram = 1·29 per cent.

Hence about 290° may be taken as the temperature of initial action.

With amorphous carbon the following numbers were obtained, the experiments being conducted precisely as described in the first report.

Temperature	360°	360—420°	420—440°	440—460°
Time in minutes	30	15	15	15
CO_2 produced	—	—	—	2·0
Other gases	—	—	—	0·8
Total gas	·25	·5	·75	2·8
Gas due to occlusion	·3	·4	·7	0·8
Gas due to reduction	Nil	Nil	Nil	2·0

Hence 450° may be taken as the temperature of initial action.

On comparing the foregoing results with those obtained with ferric oxide prepared by ignition processes described in the first report,

the following numbers are obtained as the temperatures of initial action :—

Reducing agent.	Ferric oxide.		Ferroso-ferric oxide.	Ferrous oxide.
	From ignition of $FeSO_4$.	From ignition of precipitated Fe_2O_3.		
Carbon oxide	202	220	200	275
Hydrogen	260	245	290	305
Carbon (from CO)	430	430	450	450

from which it appears that the difference in temperature of initial action of each reducing agent is hardly greater than may reasonably be ascribed to difference in physical texture due to differences with modes of preparation of the different oxides; that is, the oxides of iron, like those of copper, are first acted on by the three reducing agents, carbon oxide, hydrogen, and carbon at sensibly the same temperatures when in the same physical states, whatever the composition of the oxides; whence it probably results that the heats of combustion of iron to FeO, to Fe_3O_4, and to Fe_2O_3, are sensibly the same (calculated per equal amount of oxygen combined), just as the heats of combustion of copper to Cu_2O, and to CuO are sensibly the same (Andrews). That this is so is indicated by the values obtained by Julius Thomsen as the "heat of formation" of ferrous and ferric hydrate from iron, oxygen, and water (*Jahresbricht*, 1873, p. 81), viz., 68280 for FeO,H_2O, and 191130 for F_2O_3, $3H_2O$, or 68280, and 63710 per 16 grams of oxygen: it is noticeable that the heat of formation of the lower oxide is somewhat, but not much, greater than that of the higher one, whence the heat evolution during reduction of the first must be slightly less than that during reduction of the second; whilst accordingly, if there is any noticeable difference between the temperatures of initial action of reducing agents on FeO and on higher oxides, it is in the direction indicated by the thermal rules arrived at from the previous experiments, the FeO requiring a slightly higher temperature than the other oxides.

In the case of ferroso-ferric oxide the presence of small quantities of silicate, titanate, &c., and the denser texture produced by fusion, appears to raise considerably the temperatures of initial action of these three agents; thus the following numbers were obtained with New Zealand iron-sand picked out by a magnet after crushing and well washing to get rid of particles of dust, &c., and finally powdering finely in an agate mortar. Neither carbon oxide nor hydrogen had any action whatever on the iron-sand at the temperature of boiling mercury; both, however, acted at the temperature of boiling sulphur, weight being lost, and CO_2 being formed on passing CO over the ore

at that temperature, and a yet greater loss of weight ensuing when hydrogen was used instead of carbon oxide.

1·256 gram heated in CO for 15 minutes in sulphur vapour lost 0·0030 = 0·24 per cent.

A copious precipitate was formed in baryta-water by the exit gas.

1·0995 gram heated in H for 15 minutes in sulphur vapour lost 0·0035 = 0·32 per cent.

1·0995 gram heated in H for 30 minutes in sulphur vapour lost 0·0105 = 0·95 per cent.

It was found impracticable to obtain accurately the temperatures of initial action in these two cases; it does not follow that because at about 420° hydrogen acts somewhat more energetically than carbon oxide, therefore the initial temperature of action of hydrogen is below that of carbon oxide; for it has been noticed in other cases that the loss of weight on heating in CO to a temperature somewhat above the point of initial action takes place more slowly than in hydrogen under analogous conditions, a circumstance probably connected with the superior lightness and diffusibility of hydrogen: moreover, the following experiment indicates that the initial action of CO is really manifested at a lower temperature than that of hydrogen. A gram of finely powdered iron-sand was introduced into each of two similar tubes holding about 4 c.c., one of which was filled with CO and carefully sealed, and the other similarly filled with hydrogen and sealed: both tubes were then heated in mercury vapour for three hours. After cooling no deposition of moisture was apparent in the hydrogen tube, and no absorption took place on opening the tube under mercury; whence evidently no action had here taken place. With the other tube, however, action had evidently taken place; for on opening the tube no absorption ensued, but 25 per cent. of the contained gas had become converted into CO_2, being absorbed by potash, and precipitating baryta-water.

It is noteworthy that an analogous result as regards the effect of long continued heating to a temperature somewhat below the point of initial action as deduced from experiments lasting a few minutes only has been observed with other metallic oxides: thus cupric oxide prepared from ignition of the nitrate is not visibly acted on by pure CO during 5 to 10 minutes at temperatures below 125°; but if a large quantity of this substance be sealed up with CO and heated to 100° for several hours, a copious production of CO_2 ensues. Thus in two experiments in each of which 5 grams of this cupric oxide were sealed up with about 30 c.c. of CO, the following numbers were obtained:

After 8 hours at 100°, gas contained 70 per cent. of CO_2.
" 72 " " " 90 "

It is to be remarked, however, that the conditions were not precisely the same in the experiments for a few minutes at 125°, and those for several hours at 100°, irrespective of temperature difference: for in the first case a stream of gas at the ordinary pressure was employed, whilst in the second the pressure was increased to about $\frac{1}{3}$ atmosphere since the tubes were filled and sealed *cold*, and then heated to 100°; some experiments on the absorption of CO_2 by lead monoxide (§ 3A) indicate that increase of pressure is correlative with an alteration in rate of chemical action in such cases.

In connection with these points, we are endeavouring to obtain the data for the construction of curves representing the correlations between the deoxidation taking place with given oxides and reducing agents, the time of action, and the temperature and pressure, the other conditions being as far as possible the same.

On heating the iron-sand with carbon (from CO) it was evident that in this also a higher temperature was requisite before action commenced than with the other samples of iron oxides: the following numbers were obtained:—

Temperature	360°	360—420°	420—460° antimony well melted.	460° to about 500°, fully red-hot in daylight.
Time in minutes.....	30	15	15	15
Carbon dioxide formed	—	—	—	1·8
Other gases „	—	—	—	0·7
Total gas formed	·25	·5	about ·7	2·5
Gas due to occlusion..	·3	·4	·8	about 0·8
Gas due to reduction..	Nil	Nil	Nil	1·7

No continuous evolution of gas took place until the temperature was considerably higher than the fusion point of antimony, so that 480° at least may be taken as temperature of initial action.

The temperatures obtained with this iron-sand then are—

Carbon oxide	Between 360° and 420°.
Hydrogen.....	Ditto, but higher than with CO.
Carbon (from CO)..	About 480°.

§ 2. Oxides of Manganese.

It has just been shown that in the case of iron and copper the temperature of initial action (during some 5—30 minutes) of carbon

oxide, hydrogen, and carbon, are practically the same whatever oxide of the metal examined be employed, provided the physical state is about the same; whilst coincidently the heat evolved in converting a given quantity of oxygen into any one oxide of either metal severally is practically equal to that evolved in the formation of any other oxide of the same metal. *A priori* it would seem unlikely that the heats of formation of the higher oxides of metals, which like manganese form superoxides decomposed by heat alone and not corresponding to stable well-defined series of salts would be as great as the heats of formation of the lower oxides of these metals respectively; whilst, as shown by J. THOMSEN (*Jahresbericht*, 1873—80), the heat of formation of manganous hydrate, $MnO.H_2O$, is far greater in proportion to the oxygen employed than that of hydrated manganese dioxide, $MnO_2.H_2O$, the values being 94,770 and 116,280 respectively, or 94,770 and 58,140 per 16 grams of oxygen. It should hence result, if the rules hitherto traced out connecting the initial temperature at which an action of the form—

$$AB + C = A + BC$$

takes place be generally applicable, that the action of a given reducing agent on manganese dioxide begins to take place at a lower temperature than that at which the reducing action on the lower oxide is first noticeable. To see if this is the case, the following experiments were made, from which it clearly results that the thermic rule applies here also:—

(A.) *Precipitated Manganese Dioxide.*

Two specimens of manganese dioxide were prepared by precipitation processes; the first, by adding to solution of pure manganese chloride excess of caustic soda, adding bromine to supersaturation, leaving the solution at rest for 48 hours, and filtering off after repeated washings by decantation; the second, by boiling potassium permanganate solution with dilute nitric acid, and thoroughly washing on a glass-wool filter. Jet-black and somewhat glossy substances were obtained after drying at 100°; neither product, however, was pure manganese dioxide; for, in addition to water of hydration, a certain amount of an oxide lower than MnO_2 was present in each. Thus the following analytical numbers were obtained:—

I. *Specimen prepared by Bromine process.*—0·3615 gram heated with hydrochloric acid, and the vapours received in potassium iodide solution liberated iodine equal to 65·5 c.c. of decinormal iodine solution (titrated by thiosulphate), corresponding to 0·0524 oxygen = 14·49 per cent.

0·3885 gram corresponded to 70·9 c.c. = 0·05672 oxygen = 14·59 per cent.

0·7030 gram ignited over a gas blowpipe left 0·6110 gram of residual oxide; this, however, contained somewhat more oxygen than Mn_3O_4, since on titration by the iodine process it corresponded to 73·9 c.c. of decinormal iodine = 0·0591 gram oxygen = 9·67 per cent., whilst had it been Mn_3O_4, it would only have corresponded to 53·4 c.c. of decinormal iodine = 0·0427 oxygen = 6·99 per cent.; the amount of MnO present, therefore, was 0·6110 − 0·0591 gram = 0·5519 gram = 78·51 per cent.

0·3420 gram was heated in a current of air for several hours to 200° till perfectly constant in weight; the loss of weight was 0·0240 gram = 7·02 per cent. That no material portion of this loss was due to the evolution of oxygen was shown by titrating the residue by the iodine process, when it represented 60·7 c.c. of decinormal iodine = 0·0486 gram oxygen = 14·21 per cent. reckoned on the undried substance, or practically the same as that found before heating to 200°.

These percentages are close to those required for the formula—

$$Mn_{11}O_{20},4H_2O = 7MnO_2,2Mn_2O_3,4H_2O.$$

		Calculated.		Found.	
$11MnO$	781	78·33		78·51	
O_9	144	14·45	14·49		14·59
$4H_2O$	72	7·22		7·02	
$7MnO_2,2Mn_2O_3,4H_2O$	997	100·00			

II. *Specimen prepared from Permanganate.*—0·7510 gram ignited over a large Bunsen lamp left of residue 0·6620 gram; on repeating the ignition the residue slightly *gained* in weight, now weighing 0·6650 gram; whilst after heating almost to whiteness for 15 minutes over the gas blowpipe, the crucible being surrounded by a clay jacketting furnace, it weighed 0·6545 gram. Even this final product, however, was not Mn_3O_4, inasmuch as 0·6485 gram of it treated by the iodine process corresponded to 69·1 c.c. of decinormal iodine = 0·05528 oxygen, or 8·52 per cent.; whilst Mn_3O_4 requires 6·99 per cent. Since, however, the product of the last heating contained 100 − 8·52 per cent. of MnO = 91·48 per cent., the original dioxide employed contained $\frac{0·6545}{0·7510} \times 91·48$, or 79·73 per cent. of MnO.*

1·6725 gram in Fresenius and Will's apparatus gave by the

* In connection with these numbers and those obtained previously with the first specimen of precipitated MnO_2, indicating that the composition of the oxide obtained by igniting MnO_2 is variable, and contains more oxygen than Mn_3O_4, it is noticeable that the products obtained by strongly calcining in the air manganese carbonate and manganese monoxide, MnO, exhibit similar peculiarities. *Vide infra* § 2, C, D, and E.

oxalic acid process 1·4070 CO_2, representing 0·2558 oxygen = 15·29 per cent.

0·1965 gram corresponded to 37·6 c.c. of decinormal iodine when titrated by the iodine process = 0·03008 oxygen = 15·31 per cent.

0·5435 gram heated to 200° in a current of dry air lost 0·0230 gram, a drying tube attached gaining 0·0250 (hence, as with the first specimen, no oxygen was expelled at 200°, for otherwise the loss of weight would have *exceeded* the water collected; it is shown below that no oxygen was evolved on heating this specimen in a Sprengel vacuum to any temperature short of 260°).

0·5165 gram lost at 200° 0·0230 gram.

These percentages are close to those required for the formula—

$$Mn_{21}O_{39},5H_2O = 15MnO_2,3Mn_2O_3,5H_2O.$$

	Calculated.		Found.		
$21MnO$	1491	79·78		79·73	
O_{18}	288	15·41	15·29		15·31
$5H_2O$	90	4·81	4·23	4·60	4·45
$15MnO_2,3Mn_2O_3,5H_2O$	1869	100·00			

Comparing this formula with that arrived at for Specimen I, $7MnO_2.2Mn_2O_3.4H_2O$, it is at once evident that Specimen No. II contains a somewhat smaller quantity of oxide lower than MnO_2 than is present in No. I. For this reason Specimen II (prepared from permanganate) was chosen for the subsequent experiments detailed below; the point of initial action of hydrogen being determined by loss of weight, the substance was rendered anhydrous by heating to 200° in a current of dry air for some time, no further loss of weight ensuing on continuing the heating for an hour.

Carbon oxide was found to act vigorously on the anhydrous oxide at temperatures below 60°, whilst even at the ordinary temperature CO_2 was slowly formed, the issuing gases forming a perceptible precipitate in baryta-water; a tube containing about 20 c.c. of pure CO, and about 1·5 gram of the manganese dioxide was sealed up, and left to itself for 10 days at Christmas in a room without a fire (temperature probably from — 10° to + 10°). When opened the gases contained 32·1 per cent. of CO_2.

It is noteworthy that the non-dehydrated oxide (dried only at 100°) acted in just the same way, and not apparently any more vigorously; the other specimen of dioxide (prepared by the bromine process) behaved in precisely the same way, a perceptible precipitate being formed in baryta-water by passing pure CO over it for two or three minutes at a temperature of about 18°.

To determine the temperature at which hydrogen first began to act, weighed quantities of the dioxide dried at 200° were heated in a slow current of hydrogen precisely as above described. No loss of weight was produced by heating for 15 minutes to any temperature below and up to 140°.

0·2920 gram heated to 150° for 15 minutes lost 0·0015 gram = 0·51 per cent.

On further heating to 170° for 15 minutes this lost in addition 0·0040 gram = 1·37 per cent.

And on further heating to 190° for 15 minutes this lost in addition 0·0085 gram = 2·91 per cent.

Hence the temperature of initial action lies between 140 and 150°, and therefore is near 145°.

In another similar experiment no loss occurred at 140°, 0·48 per cent. at 150° for 15 minutes, and a further loss of 2·91 per cent. on again heating to 190° for 15 minutes.

As a further check on these numbers 0·3060 gram were heated in hydrogen to 160° for 30 minutes, whereby the loss in weight was 0·0070 gram = 2·29 per cent.

On titrating the "available oxygen" in the residue by the iodine process it was found to represent 51·9 c.c. of decinormal iodine = 0·04152 gram oxygen = 13·57 per cent. reckoned on the original substance. As the substance originally yielded by the same process 16·04 per cent., the loss of oxygen during reduction was 2·47 per cent., which agrees very fairly with the loss of weight determination.

The determination of the temperature of initial action of carbon was complicated by the circumstance that although no oxygen was evolved on heating to 200° in air, yet on heating in a Sprengel vacuum to temperatures below 360° oxygen was continuously evolved. Experiments were therefore made simultaneously with the manganese dioxide alone (0·6 gram), and the same quantity of dioxide mixed with half its weight of carbon (from CO) in the same way as those previously described with metallic oxides mixed with carbon. The following values were obtained, each pair of simultaneous experiments being exactly alike in all respects save the presence of carbon :—

(1.) Heated in mercury-vapour (360°) for 30 minutes: gas evolved reduced to 0° and 760 mm.—

	Dioxide alone.	Dioxide and carbon.
CO_2.....	Nil	7·9 c.c.
Oxygen	3·5 c.c.	0·1
Other gases ..	trace	
Total gas	3·5	8·0

(2.) Heated in air-bath to 270° for 30 minutes—

	Dioxide alone.	Dioxide and carbon.
CO_2.....	Nil	2·3
Oxygen	0·7	0·1
Other gases ..	Nil	
Total gas	0·7	2·4

(3.) Heated in air-bath to 250° for 30 minutes—

	Dioxide alone.	Dioxide and carbon.
Total gas evolved..	Nil	0·15

just that due to occlusion by the carbon.

It hence results that at a temperature between 250° and 270°, and therefore very close to 260°, this form of manganese dioxide first begins to evolve oxygen *in vacuo*, and that the action of carbon thereon is also first manifested *in vacuo* at the same temperature. That the carbon does actually act is shown by the circumstances, firstly, that in presence of carbon no free oxygen was evolved, but only carbon dioxide; and secondly, that the amount of oxygen present in the CO_2 thus formed is considerably greater in each case than that evolved in the free state in the companion experiments respectively. Thus reckoned per gram of manganese dioxide employed, the oxygen eliminated was—

	Temperature.	Evolved as CO_2.	Evolved as free O.
Exp. (I) ..	360°	0·0187 gram = 1·87 p. c.	0·0083 gram = 0·83 p. c.
„ (II) ..	270°	3·0054 „ = 0·54 „	0·0016 „ = 0·16 „

The ratios of the oxygen evolved as CO_2 and as free O in these two experiments are (since carbon dioxide occupies the same space as the oxygen contained therein)—

$$(1.)\quad \frac{7·9}{3·5} = 2·26 \text{ to } 1 \text{ at } 360°$$

$$(2.)\quad \frac{2·3}{0·7} = 3·28 \text{ to } 1 \text{ at } 270°$$

whence it would seem that the reducing action of carbon increases less rapidly from 270 to 360 than does the tendency to evolve oxygen in the free state, the increase in the former case being from 2·3 to 7·9 or from 1 to 3·43, and that in the latter from 0·7 to 3·5 or from 1 to 5·0.

On the whole, then, the temperatures of initial action of carbon oxide, hydrogen, and carbon on this manganese dioxide are—

CO	Below 15°
Hydrogen	Near 145°
Carbon.....	„ 260°

University of Michigan

or in the same relative order as that hitherto found with iron and copper oxides.

(B.) *Pyrolusite.*

A sample of finely crystallised compact pyrolusite was found on qualitative analysis to contain practically nothing but manganese, oxygen, water, and SiO_2; especially no more than traces of iron or other reducible metallic oxides were present. At 200° this substance did not become anhydrous, although it lost a little moisture; on analysis the substance dried at 200° till perfectly constant in weight gave the following numbers:—

1·4330 gram gave 0·0070 SiO_2 = 0·49 per cent.

1·1860 gram ignited in a current of dry air communicated to a calcium chloride tube 0·0420 gram H_2O.

1·2530 gram, by Fresenius and Will's process, gave 1·078 CO_2 = 0·1960 oxygen.

0·3230 gram, by the iodine process, corresponded to 63·7 c.c. of decinormal iodine = 0·05096 O.

			Mean.
SiO	0·49		0·49
H_2O	3·54		3·54
O.....	15·64	15·78	15·71
MnO (by difference)			80·26
			100·00

On calculating these numbers into percentages reckoned on the material excluding the 0·49 per cent. of SiO_2, they are found to agree with the formula $Mn_{30}O_{55}, 5H_2O = 22MnO_2,4Mn_2O_3,5H_2O$,

	Calculated.		Found.
$30MnO$	2130	80·81	80·66 (by difference)
O_{25}	416	15·78	15·78
$5H_2O$	90	3·41	3·56
$22MnO_2,4Mn_2O_3,5H_2O$..	2636	100·00	100·00

so that the natural pyrolusite had a composition closely resembling the precipitated manganese dioxide (prepared from permanganate), so far as ratio between manganese and oxygen is concerned, the anhydrous substances being indicated respectively by—

Pyrolusite, $22MnO_2,4Mn_2O_3 = 11MnO_2,2Mn_2O_3$,
Precipitated dioxide, $15MnO_2,3Mn_2O_3 = 10MnO_2,2Mn_2O_3$,

each being practically manganese dioxide, but actually containing somewhat less oxygen than pure MnO_2. The pyrolusite, however, parted with only minute quantities of combined water at 200°, the

water of hydration being only expelled at a higher temperature, whilst the water of hydration in the precipitated dioxide (not removed at 100°) was practically all lost at 200°).

The action of carbon oxide was not noticeable at any temperature below and up to 85°. At 87° a slight turbidity was produced in baryta-water on passing the gas for some few minutes, and at 95° the reducing action was very manifest.

Hydrogen did not begin to act at any temperature below and up to 180°, no loss of weight being occasioned after 15 minutes' exposure.

At 200° 1·1705 gram lost in 15 minutes 0·0005 gram = 0·04 per cent.

At 210° 1·1545 gram lost in 15 minutes 0·0075 gram = 0·17 per cent.

At 210° 1·1895 gram lost in 30 minutes 0·0075 gram = 0·63 per cent.

At 220° 1·1700 gram lost in 15 minutes 0·0100 gram = 0·85 per cent.

Hence the temperature of initial action lies between 180° and 200°, and therefore is near 190°.

In order to prove that the trifling loss of weight at 200—210° was not due to expulsion of combined water, a similar experiment was made with air instead of hydrogen; no loss of weight at all occurred. Moreover, whilst, as just stated, on heating 1·1895 gram in hydrogen to 210° for 30 minutes the loss of weight was 0·0075 gram = 0·63 per cent., on further examining by the iodine process, 0·3530 gram of the reduced substance, representing 0·3555 of the unreduced substance, it corresponded to 66·0 c.c. of decinormal iodine = 0·0528 oxygen = 14·85 per cent. As the original substance contained oxygen = 15·71 per cent., the loss on heating in hydrogen is 0·86 per cent., which fairly agrees with the loss of weight determination.

The temperature of initial action of carbon was determined in the manner above described, simultaneous experiments being made with 0·6 gram of the dioxide, and the same weight of dioxide mixed with half its weight of carbon. The following numbers were obtained:—

Temperature.	Pyrolusite alone.	Pyrolusite and carbon.
At 360° for 30 minutes	No gas evolved.	0·2 c.c. (due to occlusion).
At 420° for 15 minutes	CO_2..... Nil Oxygen .... 0·6 Other gases trace 0·6	CO_2..... 6·5 Oxygen ..... } 0·2 Other gases .... } 6·7

Hence between 360° and 420°, say at 390°, is the temperature at which reduction by carbon and evolution of free oxygen on heating alone in a Sprengel vacuum both commence, the former action being at 420° very much more powerful than the latter.

The temperatures of initial action, then, are—

Carbon oxide	87°
Hydrogen	Near 190
Carbon.....	„ 390

again following the usual order.

(C.) *Manganoso-manganic Oxides.*

With the object of preparing the oxide, Mn_3O_4, the usual process employed in the quantitative estimation of manganese was tried, perfectly pure manganous chloride being precipitated by sodium carbonate, and the resulting manganous carbonate thoroughly washed, dried, and calcined for two hours at a pretty bright red heat with frequent stirring. The brown-red powder obtained, however, did not possess the desired composition, but corresponded much more closely to $Mn_5O_7 = Mn_3O_4, Mn_2O_3$.

0·6005 gram, treated by the iodine process, corresponded to 62·4 c.c. of decinormal iodine = 0·04992 oxygen.

0·4385 gram corresponded to 46·0 c.c. = 0·0368 oxygen.

	Calculated.					Found.	
	For Mn_3O_4.			For Mn_5O_7.			
3MnO..	213	93·01	5MnO..	355	91·73		
O.....	16	6·99	O_2	32	8·27	8·31	8·39
Mn_3O_4..	229	100·00	Mn_5O_7..	387	100·00		

Another specimen of manganous carbonate furnished analogous results; the product of several hours' calcination at a full red heat over a large Bunsen burner finally contained of "available oxygen" 8·52 per cent.

By long-continued strong ignition over a powerful gas blowpipe, especially in a capsule surrounded with a clay-jacketting furnace, the substances thus prepared lost in weight, forming ultimately substances closely approximating to Mn_3O_4; thus the product of the heating of the second sample above described for three successive periods of 10 minutes each became almost constant in weight and then gave these numbers:—

0·483 gram, titrated by the iodine process, corresponded to 42·8 c.c. of decinormal iodine = 0·03424 oxygen = 7·09 per cent.

5·533 gram, titrated by the iodine process, corresponded to 47·1 c.c.

= 0·03768 oxygen = 7·07 per cent.; calculated for Mn_3O_4, 6·99 per cent.

Another specimen similarly treated finally contained 7·13 per cent.

The action of carbon oxide, hydrogen, and carbon on each of the above two substances was tried with the following results:—

(I.) Manganoso-manganic oxide, containing 8·31—8·39 per cent. of available oxygen, corresponding nearly to $Mn_3O_7 = Mn_3O_4, Mn_2O_3$.

The action of carbon oxide was first noticeable at 97° by the baryta test, the action being well defined at 110°.

Hydrogen caused no loss of weight in 15 minutes at any temperature up to and including 230°.

At 250°, 0·5575 gram lost 0·0025 gram in 15 minutes = 0·44 per cent.

At 300°, 0·4345 gram lost 0·0035 gram in 15 minutes = 0·80 per cent.

At 320°, 0·3165 gram lost 0·0045 gram in 15 minutes = 1·42 per cent.,

whence the action commenced between 230° and 250°, or at about 240°.

With carbon from CO the following numbers were obtained, 0·6 gram being heated with 0·3 of carbon as usual.

Temperature	360°	30—400° zinc not melted but softened	400—420° zinc just melted
Time in minutes.....	30	15	15
CO_2 formed.....	—	—	3·7
Other gases.....	—	—	0·1
Total gas evolved	0·25	0·4	3·8
Gas due to occlusion....	0·3	0·4	0·4
Gas due to reduction....	Nil	Nil	3·4

Hence about 410° may be taken as the temperature of initial action of carbon, that of hydrogen being 240°, and that of carbon oxide being 97°, *i.e.*, the order is the usual one.

(II.) Manganoso-manganic oxide, containing 7·07 to 7·09 per cent. of available oxygen, corresponding nearly to Mn_3O_4.

By the baryta test the action was first noticeable at 240°, being well marked at 260°; on attempting to corroborate these results by loss of weight, however, no noticeable difference in weight was perceptible after 15 minutes' heating at any temperature lower than that of boiling mercury, at which temperature 2·14 per cent. was lost in 15

minutes and 3·90 in 30 minutes. That this imperceptible variation in weight (observed at 200°, 300°, and 320°) was due to absorption of part of the CO_2 formed so as about to compensate for the loss of oxygen, is rendered highly probable by the following experiment:—0·5 gram of the manganese oxide was sealed up in a tube containing 8·0 c.c. of CO; the tube was then heated to 250° for 3 hours, and after cooling opened under mercury, the mercury rushed in filling the tube all but 2·0 c.c., of which 0·5 c.c. was absorbed by caustic potash. Hence the CO_2 formed by action at 250° had been, to a large extent, absorbed with formation of manganese carbonate; on adding dilute nitric acid to the particles of manganese oxide after the experiment effervescence was distinctly noticeable.

Hence 240° is the temperature of incipient action of CO as nearly as could be determined, but it is not at all improbable that this temperature is a little too high, the non-evolution of CO_2 at temperatures below 240° being due to its retention by the manganese oxide; the action at these lower temperatures, however, could only have been very faint, *no gain* in weight being observable.

Hydrogen brought about no loss of weight in 15 minutes at any temperature up to and including 250°.

At 260° 0·2480 gram lost in 15 minutes 0·0005 gram = 0·20 per cent.

At 280° 0·2480 gram further lost in 15 minutes 0·0020 gram = 0·80 per cent.

At 300° 0·1600 gram lost in 15 minutes 0·0055 gram = 3·44 per cent.

At 300° 0·1600 gram lost in 30 minutes 0·0085 gram = 5·31 per cent.

At 360° 0·3500 gram lost in 15 minutes 0·0200 gram = 5·71 per cent.

On sealing up in a tube about 8 c.c. of hydrogen with 0·5 gram of the manganese oxide, and heating to 250° for 3 hours, a slight absorption of hydrogen was noticeable on opening the tube, about 10 per cent. having disappeared. In a precisely similar companion-experiment in mercury vapour, however, the action was much more decided, for on opening the tube under mercury, the mercury rushed up and filled the whole tube.

Hence 255° is the temperature of incipient action, as nearly as it can be fixed.

On heating 0·6 gram of the Mn_3O_4 with 0·3 of carbon from CO, the following values were obtained:—

Temperature	360°	360—420°	420—440° Zinc melted. Antimony not melted.
Time in minutes.....	30	15	15
CO_2 formed.....	—	—	5·9
Other gases.....	—	—	0·1
Total gas evolved	0·25	0·4	6·0
Gas due to occlusion	0·3	0·4	0·4
Gas due to reduction....	Nil	Nil	5·6

Hence about 430° is the temperature of initial action of carbon.

(D.) *Manganous Oxide.*

On heating precipitated manganese dioxide to redness for several hours in a platinum boat in a gentle stream of hydrogen, it lost weight rapidly at first, becoming of a greenish-grey colour, and subsequently more slowly, gradually becoming more and more green in shade; finally a substance of an emerald green tint was obtained, resembling oxide of chromium, but of a somewhat lighter and brighter shade. On heating this product for several hours to a full red heat in hydrogen, no further loss of weight ensued, and precisely the same result was obtained on substituting carbon oxide for hydrogen; whence it is evident that the points of initial action of carbon oxide and hydrogen on the green substance lay considerably above 500—600°.

That this green substance was pure MnO was shown by determining the increase of weight on roasting for some time in the air at a red heat, and also determining the "available oxygen" in the superoxide thus formed by the iodine process: sensibly equal values were obtained, which could not have been the case had the green substance contained manganese and oxygen in any different proportion than that indicated by MnO.

	Gram.	Per cent.
0·2655 gram roasted for three-quarters of an hour at a full red heat in a small platinum capsule gained in weight	0·0240	= 9·04
On igniting over the blowpipe for five minutes it further gained.....	0·0010	= 0·37
On further calcining at full red heat for three-quarters of an hour it further gained.....	0·0035	= 1·32
	0·0285	10·73

0·2915 gram of the roasted product, corresponding to 0·2633 of original green oxide, when titrated by the iodine process, corresponded to 34·4 c.c. of decinormal iodine = 0·02752 gram of oxygen = 10·45 per cent. calculated on the original green oxide, or sensibly the same percentage as that found by direct weighing.

It is worthy of note, in passing, that the gain in weight, had M_3O_4 been formed by the roasting, would only have been $\frac{16}{3 \times 71} = 7{\cdot}51$ per 100 of MnO; the actual gain 10·45—10·73 corresponds to the composition $Mn_{15}O_{22} = Mn_3O_4, 6Mn_2O_3$, which requires 10·52 per 100.

On mixing 0·6 gram of the green monoxide with half its weight of carbon from CO, and heating in a Sprengel vacuum to various temperatures from 360° up to a full red heat continued for half an hour (the tube being almost collapsed), only 1·0 c.c. of gas was obtained, that due to occlusion by the carbon employed being, as nearly as could be estimated, exactly the same, 1·0 c.c. Moreover, the gas came off fitfully on raising the temperature from stage to stage, and not continuously. Hence the point of initial action of carbon also lies upwards of 500—600°.

On comparing the temperatures of initial action of carbon oxide, hydrogen, and carbon on these different kinds of manganese oxides, it is at once noticeable that, whilst in every case the first reducing agent begins to act at a lower temperature than the second, and the second than the third, the several temperatures of initial action are notably higher the less the oxygen in the manganese oxide.

	Manganese dioxide.		Manganoso-manganic oxide.		Manganous oxide.
	Precipitated.	Pyrolusite.			
Composition by analysis of substance regarded as anhydrous	Mn_7O_{13}	$Mn_{15}O_{28}$	Mn_5O_7	Mn_3O_4	MnO
Physical texture.....	Fine powder, amorphous	Very compact, crystalline	Fine powder, amorphous	Fine powder, amorphous	Amorphous
Carbon oxide	Below 15°	87°	97°	240°	No action at 600°
Hydrogen	Near 145°	Near 190°	Near 240°	255°	Ditto
Carbon.....	„ 260°	„ 390°	„ 410°	430°	Ditto

(E.) *Composition of the Oxide of Manganese formed by Ignition in Air of Higher and Lower Manganese Oxides.*

In the preceding sub-sections A, C, D, numbers have been quoted showing that the substances formed by the calcination at a full red heat (over a good Bunsen burner in a thin platinum capsule) of manganous oxide, manganous carbonate, or manganese dioxide, contain much more oxygen than that due to the formula Mn_3O_4. In the case of the product from manganous carbonate, half-an-hour's intense ignition over a gas blowpipe caused the expulsion of oxygen and the reduction to an oxide nearly approaching to Mn_3O_4; but in the case of manganese dioxide, conversion into Mn_3O_4 was not so nearly effected, a larger surplus of oxygen always remaining. In other experiments not quoted above, precisely similar results were obtained: thus prolonged ignition did not convert the pyrolusite employed above into Mn_3O_4, whilst another specimen of MnO roasted in the air over a Bunsen burner became a brown oxide containing 8·17 per cent. of oxygen. All the numbers obtained indicated a composition lying between Mn_3O_4 and Mn_2O_3, many of them being close to those required for the formula Mn_5O_7 or Mn_3O_4,Mn_2O_3.

Dittmar has already shown (this Journal, 1864, 294) that when manganese dioxide is ignited in air at the ordinary pressure or in a mixture of oxygen and nitrogen, in which the oxygen tension is near to that in the air (0·21 atmosphere), the oxide ultimately formed is extremely variable in composition between these limits; when, however, the oxygen tension exceeds 0·26 atmosphere, the product approximates more or less closely to Mn_2O_3, and when it falls below about 0·19 atmosphere, the product is nearer to Mn_3O_4. Thus on ignition in air at the ordinary pressure (tension of oxygen 0·21 atmosphere), Dittmar obtained in two experiments oxides MnO_x, in which $x = 1{\cdot}352$ and 1·384 respectively; the first corresponding to $4M_3O_4,M_2O_3 = Mn_{14}O_{19} = MnO_{1{\cdot}357}$; the second to $3Mn_3O_4,2Mn_2O_3 = Mn_{13}O_{18} = MnO_{1{\cdot}385}$; and on ignition in mixtures of oxygen and nitrogen in which the oxygen-tension was between 6·87 and 7·38 inches (0·23 to 0·25 atmosphere), sometimes Mn_3O_4, sometimes Mn_2O_3 predominated in the product.

The following experiment well illustrates the influence of difference of temperature on the oxide of manganese formed under otherwise constant conditions as to oxygen-tension, when that tension is 0·21 atmosphere. About $1\frac{1}{2}$ gram of manganous carbonate was calcined for an hour over a large Bunsen burner in a thin platinum capsule; the product was then roasted for some hours over the same burner, being weighed at intervals; finally the whole was strongly ignited over a blast gas furnace, and again weighed at intervals. The following numbers were obtained:—

	Gram.	Per cent.
1·4095 gram of the product of the calcination for one hour gained on further calcination for two hours	0·0055	= 0·39
After two hours more the further gain was	0·0040	= 0·29
" " "	0·0035	= 0·24
Total gain ..	0·0130	0·92

	Gram.	Per 100 of original substance.
The product was then ignited for ten minutes over the blast gas lamp, and lost	0·0125	= 0·89
Ignited ten minutes more lost further....	0·0065	= 0·46
" " "	0·0040	= 0·28
Total loss..	0·0230	1·63

The product of the last heating was found on titration to contain 7·08 per cent. of available oxygen (Mn_3O_4 requires 6·99 per cent.), whence the substance ultimately produced by the first series of calcinations over the Bunsen burner contained in 100 + 1·63 parts, 7·08 + 1·63 of "available oxygen" = 8·52 per cent., corresponding to $2Mn_3O_4,3Mn_2O_3$, which requires 8·58 per cent.

From these experiments, it results that in the quantitative estimation of manganese the usual directions of the text books to precipitate as carbonate and ignite until there is no further gain in weight may lead to serious errors, if, as is usual, an ordinary large Bunsen lamp be employed for the ignition, it being assumed that the end product is Mn_3O_4; whilst if the manganese be precipitated as hydrated peroxide and ignited, the same result may be brought about. Either a prolonged exposure of the substance to the highest temperature of a good gas blowpipe is essential to convert it into something approaching to Mn_3O_4, or preferably the "available oxygen" in the weighed calcined substance must be determined, and the true amount of MnO present thence deduced by subtraction from the total weight. The MnO present may also be obtained by prolonged heating in hydrogen at a bright red heat until weight is no longer lost, and weighing the residue. The error produced by reckoning the roasted product just described containing 8·52 of oxygen as Mn_3O_4, would amount to an over estimation of manganese to the extent of about 16 parts in the thousand, = 1·6 per cent.; for every 100 − 8·52 = 91·48 of MnO, really present would be estimated as 100 − 6·99, or 93·01 parts.

A curious phenomenon was observed with a specimen of nearly pure MnO prepared as just described, by reduction in a crucible at a bright

red heat by hydrogen. After cooling down in an atmosphere of hydrogen (the crucible being plunged into a jar of CO_2 to extinguish the flame), the product was of a tolerably fine green underneath, with a brownish film on the surface; on standing exposed to the air for a couple of days under a shade, the film became black and much thicker, whilst an increase in weight of 3·93 per cent. took place, indicating a spontaneous absorption of oxygen. Nothing of the kind was observed with pure MnO, prepared by long-continued heating of the dioxide in a boat in a current of hydrogen, until no further loss of weight ensued even after several hours' further heating; no gain in weight or alteration in appearance ensued even after several days' exposure to air. Another specimen of not quite perfectly reduced MnO, just resembling the first in appearance, was kept over sulphuric acid for a fortnight, without altering in appearance or weight; it was then freely exposed to the air under a shade for a few days without noticeable alteration; at the end of a week, however, the brownish film had become sensibly darker and thicker, and an increase of weight to the extent of 1·06 per cent. had taken place.

§ 3. Oxides of Lead.

In extension of the preceding experiments with the oxides of manganese, the following observations were made with various lead oxides:—

(A.) *Monoxide.*

Pure lead nitrate was recrystallised and ignited at first gently, and afterwards somewhat more strongly, but without fusion, until no more fumes of oxides of nitrogen were evolved. On heating the product with pure sulphuric acid, no fumes were evolved capable of acting on potassium iodide and starch; and on boiling with hydrochloric acid, and passing the vapours into potassium iodide and starch, only a trace of blue coloration was formed, showing that the lead oxide was practically free from any higher oxide. Moreover, on dissolving 0·9515 gram in glacial acetic acid, adding pure sulphuric acid, evaporating the poured off fluid to dryness, and weighing the total lead sulphate formed, 1·2920 gram of $PbSO_4$ were obtained.

	Calculated.			Found.
Pb	207	92·83		92·77
O	16	7·17	(By difference)	7·23
PbO	223	100·00		100·00

On heating this oxide in carbon oxide, it was found that a permanent change of tint from reddish-yellow to slatey-grey ensued, when even only a very minute amount of reduction had taken place, this

change of colour being accompanied by the production of a perceptible turbidity, when the partially reduced substance was dissolved in hot acetic acid (the original substances dissolved to an almost perfectly clear fluid under the same conditions). This change of colour was faintly noticeable at temperatures somewhat below those at which any appreciable formation of CO_2 or loss of weight was first discernible, and, therefore, was presumably a more delicate test of incipient reduction than these criteria, especially as it was not produced at all at any temperature when air was substituted for carbon oxide. Thus, on leading pure carbon oxide over the lead oxide for 15 minutes at a time, no change of colour took place at 155°, or below, whilst a slight change was noticeable at 160°, and a more decided alteration of tint at 170°, and much greater ones at 180° and 190° respectively. The loss of weight in 15 minutes at 160°, however, and also at 180° was less than 0·25 milligram on about 1·5 gram of substance, or less than 0·02 per cent.; whilst no appreciable turbidity was produced in baryta-water by the effluent gases. At 190° the loss of weight first became perceptible in 15 minutes, 1·228 gram losing 0·0010 gram = 0·08 per cent., the baryta test first giving a perceptible turbidity at this temperature, a very decided action being noticeable at 200°. It hence results that the temperature of incipient action during 15 minutes, as determined by the colour test, is about 160°, whilst that from the loss of weight and the baryta test lies between 180° and 190°, say at 185°. This circumstance suggests the possibility that the nascent CO_2 formed by slight action at 160°, was absorbed by the PbO, forming $PbCO_3$, so as to prevent any action on baryta-water; the fact that there was *no appreciable gain* in weight in 15 minutes, however, proves that such action, if occurring at all, was extremely slight. That the heated PbO could take up CO_2 when not in a nascent condition, although not very readily, was proved by passing CO_2 over the PbO for 15 minutes at 200°, when no alteration in weight whatever ensued; after one hour's passage of gas no alteration in weight had taken place, but after four hours' passage, 1·750 gram of PbO increased in weight 0·0020 = 0·12 per cent.; the resulting product effervesced perceptibly with dilute nitric acid, whilst the original oxide did not do so. It is especially noteworthy that the slow absorption of CO_2 by PbO at 200° thus manifest is greatly quickened by increase of pressure; thus about 2·5 grams of the same PbO was sealed up in a tube containing 10 c.c. of CO_2 at the ordinary temperature, and was then heated to 200° for four hours. On opening the tubes under mercury, the mercury rushed up, and *completely filled the tube*, indicating perfect absorption, whence it would seem that the increased pressure (about $\frac{5}{3}$ atmosphere) obtaining at first caused the action to commence sooner, and that it went on, after being once started, so thoroughly as

to render the tube vacuous, the amount thus absorbed representing about 0·0195 gram of CO_2 = 0·78 per cent. of the weight of the PbO employed. (*Vide* § 6.)

On heating the PbO in hydrogen, no alteration in tint was noticeable after 15 minutes' action at any temperature below and up to 185°, at 190° a faint change was noticeable after 15 minutes, and at 200° the change was much more decided in 15 minutes. No loss of weight was noticeable at 190° in 15 minutes, but at 200°,—

1·900 gram lost in 15 minutes 0·0010 = 0·05 per cent.
„ „ 30 „ 0·0020 = 0·10 „

Hence, manifestly, 190—195° is the temperature of initial action, both colour test and loss of weight test nearly agreeing: whence it is evident that the difference between the values for the point of initial action of CO found above by these two tests (160° and 185° respectively), is really due to the retention by the PbO of part of the first traces of CO_2 formed at the lower temperature, thus preventing any perceptible loss of weight being perceptible, and diminishing the turbidity produced in baryta-water by the issuing gas below the point at which it is readily recognisable.

Carbon first began to act at a considerably higher temperature, the following numbers being obtained with carbon from CO, and the sugar-charcoal described in the first report:—

	Sugar charcoal.			Carbon from CO.	
Temperature	360°	360—420°	420—450°	360°	360—420°
Time in minutes	30	—	—	30	15
CO_2 collected	—	—	23·4	—	27·8
Other gases	—	—	0·2	—	0·2
Total gas	0·5	0·55	23·6	0·3	28·0
Gas due to occlusion	0·5	0·53	0·6	0·3	0·5
Gas due to reduction	Nil	Nil	23·0	Nil	27·5

In the first case no action occurred until zinc was well melted and antimony was softening, so that about 435° is the temperature of initial action. In the second case, no gas was evolved until the temperature was very close to the melting point of zinc, when action began and went on rapidly, so that here about 415° is the temperature.

On the whole, then, the temperatures of initial action are:—

	By colour test.	By baryta and loss of weight tests.
Carbon oxide	160	185
Hydrogen.....	190	195
Carbon from carbon oxide	415	
Carbon from sugar.....	435	

(B.) *Plumboso-plumbic Oxide.*

A finely-coloured specimen of commercial red lead was selected which yielded on qualitative analysis nothing but lead and oxygen, with a minute trace of organic dust, which led to the evolution of a small quantity of CO_2 on heating in a Sprengel vacuum. On analysis, this yielded numbers indicating a composition much nearer to $Pb_5O_6 = Pb_3O_4 + 2PbO$ than to Pb_3O_4.

1·000 gram gave 1·230 gram of $PbCl_2$ by moistening with HCl, and evaporating down till no more gain in weight was noticed, and finally heating to fusion.

0·664 gram left after ignition 0·6530 fused PbO.

0·500 gram titrated by the iodine process represented 8·85 c.c. of normal iodine = 0·00708 oxygen.

0·500 gram titrated by the iodine process represented 8·95 c.c. of decinormal iodine = 0·00716 oxygen.

	Calculated.		Found.		Mean.
5PbO	1115	98·59	98·67	98·35	98·51
O	16	1·41	1·42	1·43	1·43
Pb_5O_6	1131	100·00			99·94

Carbon oxide did not act on this substance below 200°; at this temperature a slight action was noticeable (baryta test), whilst at 215° the action was very evident. 1·880 gram heated to 205° in CO for 15 minutes lost 0·0015 gram = 0·08 per cent.

On heating in hydrogen no loss of weight was observed at 200° nor at 220°.

At 240° 2·112 gram lost 0·0045 in 15 minutes = 0·21 per cent.
„ 250° 2·155 „ „ 0·0050 „ „ = 0·23 „

At 270° the residue from the preceding lost further 0·0080 in 15 minutes = 0·37 per cent.

Comparative experiments made with red lead alone (0·6 gram), and the same weight of red lead with half its weight of carbon (from CO), in the way described in § 2, gave the following results:—

Temperature.	Red lead alone.	Red lead and carbon.
At 200° for 15 minutes ...	No gas evolved.....	0·2 c.c. (due to occlusion
250° „ „ ...	Ditto	0·25 c.c. (ditto)
300° „ „ ...	Ditto	0·3 c.c. (ditto)
360° (mercury vapour) for 15 minutes	Gas evolved for a few minutes only CO_2 ..... 0·8 Other gases .... — 0·8	Gas continuously evolved Co_2 ..... 2·9 Other gases 0·1 3·0

The evolution for a short time of CO_2 from the red lead alone was doubtless due, as above stated, to the presence of a trace of organic dust in the red lead; the non-evolution of free oxygen alone is noteworthy, a different result being obtained with lead dioxide (*infra*) as well as with the superoxides of manganese, nickel, and cobalt. The temperature of initial action of the carbon may be taken as 330° (mean of 300° and 360°, so that the order of reduction is the usual one:—

Carbon oxide	200
Hydrogen	230
Carbon	330

(C.) *Lead Dioxide.*

The red lead used in the preceding experiments was digested with dilute nitric acid for two days, and the residual puce oxide thoroughly washed and dried at 100°, and finally at 130°. On analysis it was found to be nearly indicated by the formula $Pb_{11}O_{21}$, which may be written $19PbO_2,Pb_3O_4$ or $10PbO_2,PbO$.

0·2000 gram titrated by the iodine process represented 15·2 c.c. decinormal iodine = 0·01216 oxygen.

0·2085 gram titrated by the iodine process represented 16·0 c.c. decinormal iodine = 0·0128 oxygen.

	Calculated.		Found.		Mean.
$11PbO$	2453	93·88			
O_{10}	160	6·12	6·08	6·14	6·11
$Pb_{11}O_{21}$	2613	100·00			

On ignition, 0·6980 gram lost 0·0475 gram = 6·80 per cent; whence it would appear that a few tenths per cent. of water were still pre-

sent after drying at 130°; no loss of weight, however, took place on heating to 240°. On heating to redness in a Sprengel vacuum, no CO_2 was evolved.

Carbon oxide first began to act at 80° (baryta test), the action being well marked at 90°. 0·9655 gram at 100° for 15 minutes lost 0·0035 gram = 0·36 per cent.

Hydrogen did not begin to act at any temperature below and up to 135°.

At 150°, 1·365 gram lost in 15 minutes 0·0010 gram = 0·07 per cent.

At 170°, the residue further lost in 15 minutes 0·0050 gram = 0·36 per cent.

At 200°, 0·967 gram lost in 15 minutes 0·0120 gram = 1·24 per cent.

" " " " 30 " 0·0270 " = 2·79 "

At 240°, the residue further lost in 15 minutes 0·0120 gram = 1·24 per cent.

Hence the action began at about 140°, and was so far energetic at 200—240° that in an hour almost the whole of the "available oxygen" was removed, 5·27 per cent. being lost out of 6·11 per cent.

As a check on this initial temperature determination, 1·2195 gram was heated to 140° in hydrogen for 30 minutes, when a loss of 0·0025 gram was observed = 0·20 per cent.

0·6090 of the residue, representing 0·6105 of original substance, on titration by the iodine process, corresponded to 45·5 c.c. decinormal iodine = 0·0364 oxygen = 5·96 per cent.

0·608 of the residue, representing 0·609 of original substance, corresponded to 45·5 c.c. of iodine = 0·0364 oxygen = 5·97 per cent.

Hence the mean "available oxygen" before heating in hydrogen being 6·11 per cent., and that after 5·96 per cent., the loss was 0·15 per cent., closely agreeing with the loss of weight determination.

The temperature of initial action of carbon from CO was found as above described, comparative experiments being made with the dioxide alone (0·6 gram), and the same weight of dioxide with half its weight of carbon.

Temperature.	Dioxide alone.	Dioxide and carbon.
Heated up to 150° for 15 minutes	No gas evolved	About 0·1 c.c. (due to occlusion)
At 200° for 15 minutes ..	Ditto	About 0·15 c.c. (ditto)
250° „ „ ..	Ditto	About 0·2 c.c. (ditto)
270° „ „ ..	Gas continuously evolved CO_2 ..... Nil Oxygen .... 1·5 Other gases.. trace Total .. 1·5	Gas continuously evolved 3·0 c.c. 0·2 „ 3·2 „
360° (mercury vapour)	Gas continuously evolved CO_2 ..... Nil Oxygen .... 4·9 Other gases.. 0·1 5·0	Gas continuously evolved 8·3 c.c. 0·2 „ 8·5

Hence about 260° (mean of 250° and 270°) may be taken as the temperature at which carbon first begins to act on lead dioxide, and at which this substance begins to decompose in a vacuum, evolving oxygen. As with manganese dioxide, § 2, the formation of CO_2 causes a much more rapid withdrawal of oxygen than takes place on simply splitting up; in each case the action increases with the temperature, being roughly about three times as great at 360° as at 270° in each instance.

On comparing together the temperatures of initial action of carbon oxide, hydrogen, and carbon on the above different oxides of lead, it is evident that the dioxide is much more readily reduced than the monoxide, or the plumboso-plumbic oxide, which, being formed at a low red heat, is presumably more akin to the monoxide as regards stability.

	Monoxide.	Plumboso-plumbic oxide.	Dioxide.
Composition by analysis	PbO	Pb_5O_6	$Pb_{11}O_{21}$
Carbon oxide	160—185	200	80
Hydrogen	190—195	230	140
Carbon (from CO)	415	330	260
Carbon from sugar	435	—	—

§ 4. Oxides of Cobalt.

Commercially pure cobalt nitrate was dissolved in water, slightly acidulated, and treated with sulphuretted hydrogen; the filtrate was

boiled with a little nitric acid, and treated with excess of ammonia; the clear filtered fluid deposited on standing a mass of red crystals of a cobalt-ammonium nitrate; these were collected, dried, and ignited, at first gently, and finally very strongly. A black light powder was left, consisting essentially of cobalt monoxide, but containing a small excess of oxygen; no trace of nickel was present therein, nor of any metal save cobalt: on reduction in hydrogen this black powder furnished in two experiments 77·62 and 77·70 per cent. of cobalt, or 77·66 per cent. as the mean, $Co_{16}O_{17}$ requiring 77·63 per cent. (Co = 59). In order to obtain pure CoO from this, Russell's process (this Journal, 1863, 51) was adopted, the oxide being strongly heated over a blast lamp in a current of CO_2. It was found difficult to prevent reducing gases from the flame passing inwards and effecting further reduction of the CoO when an ordinary crucible lid was employed; but by employing a sheet of platinum foil fitting pretty tightly *inside* the crucible, and perforated with a central hole for the CO_2 tube, and keeping up a rapid current of CO_2, this difficulty was easily overcome.

0·7000 gram of the oxide finally obtained gave 0·5510 metallic cobalt on reduction in hydrogen = 78·71 per cent.

Average found by Russell = 78·59 per cent.

Calculated for CoO (Co = 59) 78·67 per cent.

From the black oxide containing 77·66 per cent. of metal, the sesquioxide was prepared by dissolving in dilute nitric acid, adding pure potash in excess, and a considerable excess of bromine, and digesting in the cold for some days; the jet-black precipitate was then washed many times by decantation, collected on a glass-wool filter, thoroughly washed, and dried at 100°; as thus obtained, the oxide formed a light black powder, which lost a small percentage of water on heating to 200° in a current of dry air, but did not part with any trace of oxygen at that temperature. After thus finally drying at 200° it gave numbers agreeing with the composition $6(Co_2O_3,H_2O),CoO$.

0·2185 gram titrated by the iodine process was equivalent to 22·15 c.c. of decinormal iodine = 0·01772 gram oxygen.

0·4225 gram = 43·15 c.c. = 0·03452 gram oxygen.

0·7580 gram gave 0·4935 metallic Co = 0·6273 CoO (Co = 59).

	Calculated.		Found.		Mean.
$13CoO$	975	82·70	82·75		82·75
O_6	96	8·14	8·11	8·17	8·14
$6H_2O$	108	9·16		By diff.	9·11
$6(Co_2O_3,H_2O),CoO$	1179	100·00			100·00

As a check on these numbers, the water produced during reduction in hydrogen was determined—

0·8930 gram gave 0·3495 gram H_2O.

0·7580 „ „ 0·2960 „

	Calculated.	Found.	
Water present as H_2O....	9·11	—	—
„ formed from CoO..	19·86	—	—
„ „ Co_2O_3	9·16	—	—
Total	38·13	39·14	39·05

Hence the substance dried at 200° was essentially monohydrated cobalt sesquioxide.

(A.) *Cobalt Monoxide.*

The action of CO on the pure monoxide was found by the baryta-test to be first manifested at 155° after 3 or 4 minutes' passage of the gas; even at 170° and upwards, however, the action was not rapid, a copious production of turbidity in baryta-water by a few bubbles of issuing gas being only caused at about 180°. 0·8155 gram heated in CO to 155° for 15 minutes, lost 0·0010 gram = 0·12 per cent., no loss of weight being experienced at 100°, 120°, and 150° in 15 minutes in each case.

The action of hydrogen, on the other hand, was imperceptible at 155° and also at 160° after 15 minutes, but was quite noticeable at 170°; so that 165° may be taken as the temperature of initial action; distinctly above the temperature of initial action of CO, but only slightly above, when tested in the same way, by loss of weight.

0·8190 gram	at	160°	lost in	15	minutes	Nil = 0
„	„	170°	„	15	„	0·0010 = 0·12 per cent.
0·9400	„	180°	„	15	„	0·0030 = 0·32 „
„	„	„	„	30	„	0·0080 = 0·85 „
„	„	„	„	45	„	0·0105 = 1·12 „
0·9360	„	210°	„	15	„	0·0075 = 0·80 „
„	„	„	„	30	„	0·0105 = 1·12 „

With carbon (from CO) the following numbers were obtained, 0·6 gram of the oxide and 0·3 of carbon being employed as in all the other experiments:—

Temperature	360°	360—420°	420—440°	440—460°
Time in minutes	30	15	15	15
CO_2 produced.....	—	—	—	11·1
Other gases	—	—	—	0·9
Total gas	0·3	0·4	0·6	12·0
Gas due to occlusion ..	0·3	0·4	0·7	0·8
Gas due to action	Nil	Nil	Nil	11·2

Hence about 450° is the temperature of initial action.

(B.) *Cobalt Sesquioxide.*

By the baryta-water test, the action of CO on the cobalt sesquioxide prepared as above described, was not only readily perceptible at the temperature of the laboratory, but also at 0°, and could even be distinctly noticed after two or three minutes' passage of gas in a freezing mixture at −11°.

Hydrogen, however, did not cause any loss of weight in the substance (dried till constant in a current of air at 200°) below 110°.

0·5380 gram at 100° for 15 minutes lost nil = 0.

0·5380 gram at 120° for 15 minutes lost 0·0005 = 0·55 per cent.

0·5380 gram further heated to 135° for 15 minutes lost further 0·0030 = 0·55 per cent.

0·6905 gram at 170° for 15 minutes lost 0·0785 = 11·36 per cent.

To make doubly sure that the loss at 120° was not due to the expulsion of water of hydration, 0·6285 gram were heated in hydrogen to 125° for 30 minutes, the loss of weight being 0·0030 gram = 0·48 per cent. On titrating the residue by the iodine process, it was found to be equivalent to 59·1 c.c. of decinormal iodine, corresponding to 0·04728 gram oxygen = 7·52 per cent.; as the original sesquioxide contained 8·14 per cent. of extra oxygen, the loss deduced from the titration is 8·14—7·52 = 0·62 per cent., agreeing as nearly as could be expected with the loss of weight determination, and clearly indicating that oxygen was actually removed.

The temperature of initial action of carbon was determined as described in § 2; it was found that, just as with manganese and lead dioxide, the temperature of initial action is practically identical with that at which oxygen is first evolved: the following values were obtained, 0·6 gram of Co_2O_3 being used in each case, alone in the first instance, mixed with 0·3 gram of carbon (from CO) in the second:—

At 200° for 15 minutes..	No gas evolved	0·1 c.c. evolved (due to occlusion by carbon)
At 250° for 15 minutes.	Nil.....	0·15 c.c. evolved (due to occlusion)
At 270° for 15 minutes.	CO_2 evolved .. — Oxygen .... 5·2 c.c. Other gases .. 0·2 „ Total.. 5·4 „	5·0 c.c. 0·5 „ 0·2 „ 5·7 „

Hence about 260° is the temperature of initial action.

On contrasting the numbers obtained as above described with cobalt monoxide and sesquioxide, the same result is distinctly noticeable, as was observed with manganese oxides, viz., that each reducing agent respectively begins to act at a considerably lower temperature on the higher than on the lower oxide. Thus:—

	Monoxide.	Sesquioxide.
CO.....	155	Below −11°
H	165	110
Carbon	450	260

It may be noticed that the temperature of initial action of CO and H were determined on the cobalt oxide prepared by ignition of the cobalt-ammonium nitrate (indicated nearly by $Co_{16}O_{17}$), with the following results:—

Carbon oxide .... 120° (baryta-water test).
Hydrogen ..... 195° (loss of weight test).

In this case the difference between the temperatures for CO and H is not so small as with the pure CoO, whilst the usual rule is obeyed that CO begins to act at a lower temperature than hydrogen.

§ 5. Oxides of Nickel.

Pure nickel oxide was prepared from commercially pure nitrate by acidulating and treating with sulphuretted hydrogen, boiling the filtrate with nitric acid and adding ammonia in large excess: to the blue clear filtrate clear solution of pure oxalic acid was added in quantity insufficient to neutralise completely; on standing, nickel oxalate separated; this was collected and washed, dried and ignited, and the residue moistened with nitric acid and again ignited. In this way an oxide was formed approximating to the monoxide, more closely indicated by $Ni_{20}O_{21}$ (Ni = 59); on reduction in hydrogen it furnished 77·80 per cent. of nickel, whilst $Ni_{20}O_{21}$ requires 77·83 per cent. This oxide contained no trace of cobalt, or of any other metal save nickel.

By Russell's process (this Journal, 1863, 51) the pure monoxide was prepared from this substance (by strong ignition over a blast amp in a crucible surrounded with a clay jacket): as with cobalt monoxide, it was found necessary to avoid entrance of reducing gases by employing a crucible lid fitting *inside* the crucible, with a current of carbon dioxide led in through a perforation in the lid.

0·6705 gram of the oxide finally obtained gave 0·5270 metallic Ni = 78·60 per cent.

Average found by Russell 78·59 per cent.

Calculated (Ni = 59) 78·67 per cent.

From the nickel oxide containing 77·80 of metal we attempted to prepare the sesquioxide in the same way as that employed for cobalt sesquioxide (§ 4), viz., by dissolving in nitric acid, adding excess of pure potash and a large excess of bromine, and digesting in the cold for some days: a jet-black powder was thus obtained which, after thorough washing by decantation and on a glass-wool filter, became constant in weight at 100°, forming a hydrated substance containing considerably less oxygen than Ni_2O_3; on heating to 150° it readily parted with oxygen, but none was evolved at 140°; the oxygen evolved at 150° contained a little CO_2, indicating the presence of organic matter in small quantity (taken up from the wash-water, &c.).

0·4740 gram of product, dried at 100° till perfectly constant in weight, was titrated by the iodine process and found equivalent to 20·55 c.c. of decinormal iodine = 0·01644 oxygen.

0·4810 gram = 20·9 c.c. of iodine = 0·01672 oxygen.

0·9355 gram gave 0·5440 metallic Ni = 0·6915 NiO.

These percentages approximate to $2Ni_2O_3,5NiO,12H_2O$.

	Calculated.		Found.	
$9NiO$	675	73·13	73·92	
O_2	32	3·47	3·47	3·48
$12H_2O$	216	23·40		
$2Ni_2O_3,5NiO,12H_2O$ ..	923	100·00		

So that this body was hydrated sesquioxide largely intermixed with monoxide.

(A.) *Pure Nickel Monoxide.*

The action of CO, as determined by baryta-water, was first manifest at 120°, being very evident at 130°.

Hydrogen caused no loss of weight below or at 215°.

At 225° 0·7310 gram lost in 15 minutes 0·0010 gram = 0·13 per cent.

At 250° 0·6515 gram lost in 15 minutes 0·0095 gram = 1·45 per cent.

At 270° 0·6420 gram lost in 15 minutes 0·0560 gram = 8·72 per cent.

Carbon (from CO) gave the following numbers, 0·6 gram of oxide and 0·3 of carbon being employed as in the other experiments:—

Temperature	360°	360—420°	420—440°	440—460°
Time in minutes	30	15	15	15
CO_2 evolved	—	—	—	3·8
Other gases evolved	—	—	—	0·2
Total	0·25	0·5	0·7	4·0
Gas due to occlusion....	0·3	0·4	0·7	0·8
Gas due to action	—	—	—	3·2

Hence the temperatures of initial action of CO, H, and C are respectively about 120°, 220°, and 450°, or not very far from those found for the similarly prepared cobalt monoxide; it is noticeable that the nickel oxide containing 77·80 per cent. of metal ($Ni_{20}O_{21}$) gave as temperatures of initial action of CO and H respectively 180° and 215°, the action of the CO being but slow, even at 200°, so that only a few tenths per cent. were lost in half an hour at that temperature.

(B.) *Nickel Sesquioxide.*

The sesquioxide containing monoxide, above described, did not form CO_2 on leading CO over it at the ordinary temperature, but baryta-water began to be rendered turbid by the issuing gas at 30°, the action being well marked at 45°. Hydrogen caused no loss of weight at 60° or any temperature below that point.

At 70° 0·4935 gram lost in 15 minutes 0·0010 gram = 0·20 per cent.

At 90° 0·4935 gram further lost in 15 minutes 0·0060 gram = 1·21 per cent.

At 110° 0·4935 gram further lost in 15 minutes 0·0110 gram = 2·23 per cent.

So that about 65° is the temperature of initial action as deduced from the loss of weight test; to make sure that this loss of weight was really due to removal of oxygen and not of water of hydration, 0·5720 gram was heated to 80° for 50 minutes in a current of hydrogen, whereby a loss of weight took place of 0·018 gram = 3·15 per cent.

On titrating the residue by the iodine process it corresponded to 11·2 c.c. of decinormal iodine = 0·00896 oxygen = 1·56 per cent.; as the original substance yielded 3·48 per cent. of oxygen by titration, the loss of oxygen by reduction was 3·48 −1·56 = 1·92 per cent.

Hence oxygen was actually removed, the somewhat higher value found by loss of weight being doubtless due to loss of a little water in addition.

With carbon (from CO) the following numbers were obtained, 0·6 gram of the oxide being heated in one tube, and 0·6 gram of oxide with 0·3 of carbon in another tube simultaneously:—

	Nickel oxide alone.	Nickel oxide with carbon.
At 120° for 15 minutes	No gas evolved	Only a trace of gas, due to occlusion.
At 140° for 15 minutes	No gas evolved	Ditto.
At 150° for 15 minutes	A little gas evolved at first, and then a much slower steady evolution of oxygen.	Gas evolved continuously throughout the 15 minutes.
	CO_2 ..... 1·6 cc.	4·2 c.c.
	Oxygen .... 1·7 „	0·2 „
	Other gases .. —	trace
	Total .... 3·3	4·4

As above stated, apparently a minute quantity of organic matter was contained in the nickel superoxide, giving rise to the evolution of CO_2 on heating alone; manifestly the evolution of oxygen and the temperature of initial action of carbon lie close together at near 145°.

On contrasting the temperatures of initial action of CO, H, and carbon on these two nickel oxides, it is at once noticeable that they follow the same rule as with the oxides of manganese, lead, and cobalt, viz., that the higher oxide is first affected at a sensibly lower temperature.

	Pure monoxide.	Superoxide.
CO	120	30
H	220	65
C	450	145

§ 6. Absorption of CO and CO_2 by Metallic Oxides.

In § 2 it was incidentally noticed that when an oxide of manganese approximating in composition closely to Mn_3O_4 was heated to 250° for three hours in a sealed tube containing CO, a considerable absorption took place, manganous carbonate being formed together with a small quantity of free CO_2. This action may apparently be due to one or both of two slightly different causes; either the CO becomes directly united to the manganese superoxide forming carbonate, thus—

$$(1.)\quad Mn_3O_4 + CO = 2MnO + MnCO_3.$$

or the formation of carbonate takes place in two stages, the Mn_3O_4 being first reduced to MnO, thus—

$$(2.)\quad Mn_3O_4 + CO = CO_2 + 3MnO,$$

and the MnO thus formed subsequently combining with the CO_2 liberated, forming carbonate, thus—

$$(3.)\quad MnO + CO_2 = MnCO_3.$$

That certain anhydrous metallic oxides are capable of uniting with dry CO_2, forming carbonates, is a well-known fact; in § 3 it has been shown that in the case of PbO the absorption of CO_2 is facilitated by sealing up in a tube, and heating so that at first the tension of the CO_2 is greater than that of the atmosphere; for in two experiments in which PbO was heated to 200° for four hours in CO_2, in the one case in a gentle current of the gas, in the other in a sealed tube, the amounts of gas absorbed were respectively 0·12 and 0·76 per cent. of the weight of the PbO, the latter percentage being manifestly less than the PbO would have absorbed had the supply of CO_2 not been necessarily limited by the conditions of the experiment.

In order, if possible, to throw some light as to the true cause of the formation of manganous carbonate in the above-cited experiment, the following trials were made: that the reaction represented by equation (1) does not represent the whole chemical change is manifest from the presence of free CO_2 in residual gas.

(A.) Pure MnO was sealed up in a tube with pure CO_2 (about 0·8 gram of MnO and 10 c.c. of CO_2 being employed), and the whole heated to 250° for four hours. After cooling no inrush was perceptible on opening the tube under mercury, and no effervescence of the manganese oxide was perceptible on adding nitric acid; whence, apparently, reaction (3) did *not* take place; hence, if the second view above referred to be correct, the combination of MnO and CO_2 to form $MnCO_3$ must be greatly facilitated by both substances being in the nascent state.

(B.) Precipitated MnO_2 was sealed up in a tube with a quantity of CO insufficient to reduce the MnO_2 to Mn_3O_4 by the reaction—

$$3MnO_2 + 2CO = Mn_3O_4 + 2CO_2,$$

and the whole laid by for a fortnight in a cold room in winter time (temperature about 0—10° throughout). On opening the tube no inrush ensued, but on examination almost the whole of the CO was found to have been converted into CO_2; the manganese oxide formed did not effervesce with nitric acid. Hence the following reaction—

$$(4.)\quad MnO_2 + CO = MnCO_3,$$

parallel to equation (1) did *not* take place.

(C.) Precipitated MnO_2 was heated to 100° for three hours in a current of pure CO; reduction took place copiously, the loss in weight being 6·7 per cent., the residual oxide contained no trace of carbonate, but evolved chlorine on heating with hydrochloric acid. Here, again, reaction (4) did *not* take place.

Hence it results that there is no reason for supposing that the formation of $MnCO_3$ from Mn_3O_4 and CO is due to the direct combination of CO with a superoxide of manganese as indicated by equations (1) and (4); the more probable explanation being that equations (2) and (3) express the changes, (3) only taking place with *nascent* MnO and CO_2.

As the nascent state is not requisite for the combination of PbO and CO_2 to form $PbCO_3$ corresponding experiments were made with oxides of lead.

(D.) 2·5 grams of PbO were sealed up with 10 c.c. of pure CO at the ordinary temperature, and were then heated to 200° for four hours. On opening the tube an absorption of gas to the extent of 2 c.c. was observed, the residual gas being CO with no trace of CO_2; the lead oxide effervesced with nitric acid. In this case, therefore, every portion of CO_2 formed was absorbed by the lead oxide with formation of lead carbonate, thus—

$$(5.)\quad PbO + CO_2 = PbCO_3.$$

(E.) On repeating the last experiment with the red lead described above (§ 3) indicated by Pb_3O_6, 2·5 c.c. of gas were absorbed with formation of carbonate by 2·4 grams of red lead; 7·5 c.c. of gas left unabsorbed consisted of CO with no trace of CO_2; the residual lead oxide effervesced with nitric acid. Here, therefore, the carbonate may be supposed to be formed either by reduction to PbO and absorption of the CO_2 formed in accordance with equation (5), or by direct combination, thus—

$$(6.)\quad Pb_3O_6 + CO = 4PbO + PbCO_3,$$

this latter view, is however, rendered improbable by the result of the following experiment:—

(F.) 1·2 gram of the PbO_2 above described (§ 3) was heated in a sealed tube with about 10 c.c. of pure CO to 100° for four hours. On opening the tube no absorption was evident, and no effervescence of the resulting lead oxide was noticeable on treatment with nitric acid; 2 c.c. of free CO_2 were, however, formed. Hence it would appear to result (since the amount of reduction taking place was insufficient to reduce the PbO_2 to Pb_3O_4, and *à fortiori* insufficient to reduce it to Pb_3O_6 or PbO) that CO_2 is not absorbed by superoxides of lead under the conditions of these experiments, although it is readily absorbed by

PbO under these conditions. That this is so is made evident by the following two experiments:—

(G.) 1·2 grams of PbO_2 and about 10 c.c. of CO_2 were sealed up together, and heated to 100° for four hours. No trace of absorption nor of formation of lead carbonate was noticeable.

(H.) Precisely similar negative results as regards absorption and formation of carbonate were obtained on heating 2·5 grams of red lead and 10 c.c. of CO_2 to 200° for four hours.

On the whole, then, these experiments point to the conclusion that when a carbonate is formed by heating a manganese or lead superoxide in CO (which does not take place with all the superoxides of these metals, but at most only with those intermediate between monoxide and dioxide) the action that takes place is not a direct combination of CO and the superoxide, but is accomplished in two stages, monoxide being first formed, and this substance subsequently combining with the CO_2 thus produced, the combination taking place in the case of manganese only when the monoxide and CO_2 are nascent.

Another conclusion that may be drawn also is that the red lead indicated by the formula Pb_5O_6, was *a definite and distinct oxide of lead, and was not a mixture* of Pb_3O_4 and 2PbO, as might be supposed; for in the latter case an absorption of CO_2 must have taken place in experiment (H).

§ 7. Conclusions.

From the results detailed in Parts I and II of these researches the following general conclusions may be drawn:—

(1.) Whilst differences in physical state are attended with correlative differences in the temperatures at which the actions of the reducing agents, CO, H, and C, on metallic oxides are first manifest (after periods not exceeding a few minutes up to 15 minutes or so), the variations in temperature of initial action thus observable are usually not so great as to interfere seriously with the drawing of certain inferences, especially when the substances compared are in approximately the same physical state, having been prepared by analogous processes.

(2.) In the case of the oxides of the metals iron and copper, which form different oxides, each corresponding with definite series of salts and other compounds, and stable (*i.e.*, not evolving oxygen) on heating, the temperature of initial action of a given reducing agent on all the oxides of any one metal is sensibly the same unless the difference in physical structure is very marked; this fact is clearly correlated with the sensible equality in heat-evolution by the union of a given

quantity of oxygen with either of these metals respectively, whether the one or the other oxide be formed.

(3.) In the case of the oxides of the metals, manganese, lead, nickel, and cobalt, which form superoxides, not corresponding with definite series of salts and other compounds, and not stable on heating (*i.e.*, evolving oxygen when heated), the temperature of initial action of a given reducing agent on the superoxide of one of these metals is sensibly lower than that of the same agent on the stable monoxide of the same metal, even after making all probable allowance for difference in physical structure: in the case of manganese this fact is clearly related to the circumstance that the heat-evolution in uniting a given quantity of oxygen with the metal so as to form the superoxide, is sensibly less than the heat-evolution taking place when the monoxide is formed instead; probably, therefore, the same relationship also holds in the case of lead, nickel, and cobalt.

(4.) In no case out of many examined has any exception been found to the general rule, that the temperature of initial action (during a few minutes) of carbon oxide on a given metallic oxide is lower than that of hydrogen on the same sample of metallic oxide; and that the temperature of initial action of hydrogen is similarly lower than that of carbon on the same sample of metallic oxide. In some few cases, however, the differences between the temperatures of initial action of carbon oxide and of hydrogen are not very large.

(5.) In one or two instances at present examined, a long continued exposure of a metallic oxide to the action of a given reducing agent at a temperature some degrees lower than the temperature of initial action deduced from experiments lasting a few minutes only, will give rise to a sensible reduction of the metallic oxide, especially under an increased pressure in a sealed tube. It is therefore desirable that experiments should be made to find out how far the elements of time and pressure can be substituted for increase of temperature in such cases; on these points experiments are in progress. It is noticeable in this connection that in certain instances the rapidity of action of hydrogen appears to augment more rapidly with a slight rise of temperature than is the case in corresponding experiments with carbon oxide; a circumstance doubtless connected with the superior lightness and diffusibility of hydrogen.

(6.) In a large number of cases the rule holds that the greater (algebraically) the heat-evolution during the performance of a reaction of the kind indicated by the symbols—

$$AB + C = A + BC,$$

(when AB is a metallic oxide and C a reducing agent) the lower is the temperature at which this action is first manifested to a just

measurable extent in the course of a few minutes. All the cases included in paragraph 4 and some of those in paragraph 3 of these conclusions, are special cases of this rule; whilst probably all the other cases included in paragraph 3 also come under the rule, although it cannot be said with certainty that they do, from want of determinations of the actual heat-evolutions, or of the data from which they can be calculated.

(7.) Whilst experimenting on the above points, it has incidentally been found that the products of ignition in air of manganese carbonate and of various oxides of manganese always contain more oxygen than Mn_3O_4, and can be reduced nearly to that composition, only by long continued heating over a powerful blast-lamp; and that in consequence serious errors are apt to be introduced into quantitative determinations of manganese unless special care be taken to avoid them.

(8.) Evidence has also been obtained, tending to show that under certain conditions carbon oxide can apparently combine directly with certain metallic superoxides to form carbonates; but that the reaction really takes place in two stages, viz., first, reduction to monoxide with formation of CO_2, and second, combination of monoxide with CO_2 to form carbonate.

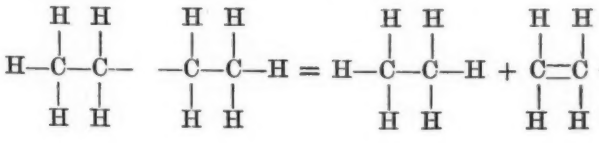
LXI. *Note on the Constitution of the Olefine produced by the Action of Zinc upon Ethylic Iodide.*

By E. Frankland, D.C.L., F.R.S., and Leonard Dobbin, Esq.

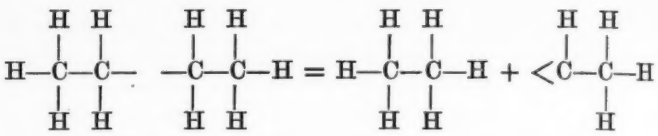
As long ago as the year 1849 (*Jour. Chem. Soc.*, vol. ii, p. 277), it was proved by one of us that the olefine produced by the splitting of ethyl at the moment of liberation from its iodide, has the formula C_nH_{2n}, and that the value of n in this formula is 2; but the constitution of the gas has never been ascertained. The equation—

$$(C_2H_5)_2 = C_2H_6 + C_2H_4,$$

expressing the transformation of ethyl into ethylic hydride and the olefine C_2H_4 admits of the two following interpretations:—



and



If the transformation occurred according to the first of these equations, the olefine would be *ethylene*, and if according to the second, *ethylidene*. We endeavoured to decide between these two interpretations by combining the olefine with chlorine and ascertaining the boiling point of the compound: for ethylenic chloride boils at 82·3° C. (Regnault) or 84·6 (Dumas), whilst ethylidenic chloride boils, according to Geuther (*Ann. Ch. u. Pharm.*, Bd. cv, 323) at 60° C.

The gas accumulated in an iron digester during the decomposition of ethylic iodide by zinc was led, in a slow stream, first through a Woulf's bottle and pumice column containing alcohol, to absorb the vapour of ethylic iodide, then through concentrated sulphuric acid to absorb alcohol vapour, and lastly, through a long bulbed tube containing several ounces of antimonic chloride. After many litres of the gas had passed, the contents of the tube containing antimonic chloride were mixed with water and submitted to distillation in a water-bath. The distillate consisted of a heavy oily layer and a lighter aqueous one. The former was separated, dried over calcic chloride, and rectified. Its boiling point was then determined by Chapman Jones's method (*Jour. Chem. Soc.*, 1878, p. 175). It behaved like a homogeneous liquid, and boiled under a pressure of 760 mm. at 83° C.

The olefine produced by the action of zinc upon ethylic iodide is therefore ethylene, and the isolation of ethylidene still remains to be accomplished, all attempts to separate this radical from its compounds having hitherto failed.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY,

SESSION 1877–78.

November 1st, 1877.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On some Hydrocarbons obtained from the Homologues of Cinnamic Acid, and on Anethol and its Homologues:" by W. H. Perkin.

"On two New Methods for estimating Bismuth Volumetrically:" by M. M. P. Muir.

"On the Oxidation of Ditolyl;" by T. Carnelley.

"Note on a New Manganese Reaction:" by J. B. Hannay.

November 15th, 1877.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On some Points in Chemical Dynamics:" by C. R. A. Wright and A. P. Luff.

"On the Chemistry of Cocoa Butter," Part I. "Two New Fatty Acids:" by C. T. Kingzett.

"On the Influence exerted by Time and Mass in certain Reactions in which Insoluble Salts are produced:" by M. M. P. Muir.

December 6th, 1877.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On Gallium:" by W. Odling.

"On Nitrification, a Report of Experiments conducted in the Rothamsted Laboratory:" by R. Warington.

"On Potable Waters:" by E. J. Mills.

"On some Derivatives of Allylacetone:" by J. R. Crow.

"On a Fourth Method for Estimating Bismuth Volumetrically:" by M. M. P. Muir.

"On the Gas of the Grotta del Cane:" by T. G. Young.

"Note on Tetrabromide of Tin:" by T. Carnelley and L. O'Shea.

December 20th, 1877.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On the Bromoderivatives of Camphor:" by Dr. Armstrong and Mr. Matthews.

"On the Action of Iodine on Camphor:" by Dr. Armstrong and Mr. Eastrell.

"On the Constitution of Terpenes and Camphor:" by H. E. Armstrong.

"On the Hydrocarbons obtained from *Pinus sylvestris*, with remarks on the Constitution of the Terpenes:" by W. A. Tilden.

"On Citric Acid as a Constituent of Unripe Mulberry-juice:" by C. R. A. Wright and G. Patterson.

"On Cuprous Chloride and the Absorption of Carbonic Oxide and Hydrochloric Acid Gas:" by J. W. Thomas.

January 17th, 1878.

Professor Odling, Vice-President, in the Chair.

The following papers were read:—

"On the Luminosity of Benzol when Burnt with Non-luminous Combustible Gases:" by E. Frankland and L. T. Thorne.

"On the Action of Reducing Agents on Potassium Permanganate:" by F. Jones.

"On the Action of Sulphuric Acid on Copper:" by Spencer Pickering.

"On the Analysis of Sugar:" by G. Jones.

"On the Decomposition-products of Quinine:" by W. Ramsay.

February 7th, 1878.

Dr. J. H. Gladstone, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

T. C. Clowd, South Australia: G. F. Doudeswell, Wimbledon; A. Ginders, Normanton; H. R. Hind, Queen's-road, S.E.; J. Woodland, Mary-le-bone, N.W.; S. P. Pickering, Bryanstone-square; T. F. Harris, Kilburn Park, N.W.; G. H. Spring, Tiverton, Devon; W. J. Williams, New Wandsworth; G. S. Taylor, St. John's Wood, N.W.; A. Lumell, Barnes, S.W.; J. V. Elsden, Hertford; A. H. Elliott, New York; C. B. Fox, Chelmsford; A. Jamieson, Camden-road, N.W.; A. H. Hooker, Lessness Heath, Kent; D. A. Louis, Great Prescott-street, E.; W. Watson, Rochester; W. H. Ellis, Toronto, Canada; J. Hadkinson, Liverpool; W. D. Harland, Manchester; H. B. Nason, Göttingen; G. Kühnemann, Dresden; R. Bodmer, Ebbw Vale; G. E. Stodart, Cambridge. E. C. Gill, South Hampstead, was elected an Associate.

The following papers were read:—

"On the Alkaloïds of the Aconites," Part II. "On the Alkaloïds contained in *Aconitum ferox*:" by C. R. A. Wright and A. P. Luff.

"Notes on the Tannins:" by B. H. Paul and C. T. Kingzett.

"On the Estimation of Phosphorus in Iron and Steel:" by E. Riley.

"An Inquiry into the Action of the Copper-Zinc Couple on Alkaline Oxy-salts:" by J. H. Gladstone and A. Tribe.

"On a New Method for the Determination of Boiling Points:" by W. Jones.

February 21st, 1878.

Dr. J. H. Gladstone, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

L. T. Wright, Beckton, E.; W. Hudson, Twickenham; T. Lichtenstein, Victoria Docks, E.; G. S. Johnson, Savile-row, W.; W. B. Lowe, Cambridge.

Mr. J. Y. Buchanan gave a Lecture "On Laboratory Experiences on board the Challenger."

March 7th, 1878.

Dr. J. H. Gilbert, Vice-President, in the Chair.

The following papers were read:—

"On some New Derivatives of Anisoïl:" by W. H. Perkin.

"Note on the Action of Ammonia on Anthrapurpurin:" by W. H. Perkin.

"On certain Polyiodides:" by G. S. Johnson.

"On an Improved Form of Wash-Bottle:" by T. Bayley.

"On the Preparation of Glycollic Acid:" by R. T. Plimpton.

March 21st, 1878.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On Aromatic Nitrosamines:" by Otto Witt.

"On a New Process for the Volumetric Estimation of Cyanides:" by J. B. Hannay.

"On certain Bismuth-compounds," Part VII: by M. M. P. Muir.

March 30th. (Anniversary Meeting.)

See pp. 221—244.

April 4th, 1878.

Dr. J. H. Gladstone, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

R. H. C. Nevile, Grantham; R. H. Jude, Maidstone; T. H. Norton, Paris; A. K. Huntington, Hampstead; G. H. Rutter, Euston-road, N.W.; S. S. Morris, Dolgelly; J. Spencer, Keighley; T. W. Drinkwater, Edinburgh; A. N. Pearson, Kensington, W.; W. T. MacAdam, Edinburgh; W. A. H. Naylor, Holborn, W.C. J. Tcherniak, Paris; M. Zingler, Belsize Park, N.W.; S. A. Goldschmidt, New York.

Mr. H. C. Sorby, F.R.S., gave a Lecture "On the Application of the Microscope to some Special Branches of Chemistry."

April 18th, 1878.

W. Crookes, F.R.S., Vice-President, in the Chair.

The following papers were read:—

"On Terpin and Terpinol:" by W. A. Tilden.

"The Poisonous Principle of *Urechites suberecta*:" by J. J. Bowrey.

"On the Temperature at which some of the Alkaloïds, &c., Sublime, as Determined by an Improved Method:" by A. W. Blyth.

May 2nd, 1878.

Dr. J. H. Gladstone, President, in the Chair.

Mr. Sydney H. Vines delivered a Lecture "On the Chemical Aspects of Vegetable Physiology."

May 16th, 1878.

Dr. J. H. Gladstone, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

J. W. Knights, Cambridge; J. H. Wilson, Calcutta; H. R. Smith, Highbury, N.; G. A. George, Dorchester; F. Slinger, York; W. Jago, Brighton; H. W. Jones, Birmingham; A. E. Tucker, Dalston, N.; B. Gregory, Blackpool.

The following papers were read:—

"On the Detection and Estimation of Free Mineral Acids in various Commercial Products:" by Peter Spence and A. Esilman.

"On the Action of Hypochlorites on Urea:" by G. H. Fenton.

"On the Behaviour of Metallic Solutions with Filter Paper, and on the Detection of Cadmium:" by T. Bayley.

"On Essential Oil of Sage:" by S. Siguira and M. M. P. Muir.

"On the Action of Bromine on Sulphur:" by J. B. Hannay.

"On the Determination of High Boiling Points:" by T. Carnelley and W. C. Williams.

"On High Melting Points," Part IV: by T. Carnelley.

June 6th, 1878.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"Analogies between the Action of the Copper-Zinc Couple and

Occluded and Nascent Hydrogen:" by J. H. Gladstone and A. Tribe.

"On the Alkaloïds of the Aconites," Part III: by C. R. A. Wright and A. P. Luff.

"On the Alkaloïds of the Veratrums," Part I. Alkaloïds of *Veratrum Sabadilla:*" by C. R. A. Wright and A. P. Luff.

"On the Action of Hydrochloric Acid on Chemical Compounds:" by J. W. Thomas.

"On the Action of Oxides on Salts:" by E. J. Mills and D. Wilson.

"On a New Test for Glycerin:" by A. Senier.

"On Ammonium Triiodide:" by G. S. Johnson.

June 20th, 1878.

W. Crookes, Vice-President, in the Chair.

The following gentlemen were elected Fellows of the Society:—

E. R. Budden, Acton; C. T. Macadam, Brixton; W. R. Criper, Devon.

The following papers were read:—

"Contributions to the History of the Naphthalene Series (No. II β-Naphthaquinone):" by J. Stenhouse and C. E. Groves.

"On Pyrotritartaric and Carbopyrotritartaric Acids:" by G. Harrow.

"On the Action of Alkaline Hypobromite on Ammonium Salts, Urea, and Oxamide:" by W. Foster.

"Action of the Halogens at High Temperatures on Metallic Oxides:" by C. F. Cross and S. Siguira.

"On Manganese Tetrachloride:" by W. W. Fisher.

"On Salts of Nitrous Oxide:" by A. E. Menke.

"Notes on Madder Colouring Matters:" by E. Schunck and H. Rœmer.

"On the Occlusion of Hydrogen by Copper:" by G. S. Johnson.

"On the Part played by Carbon in Reducing the Sulphates of the Alkalis:" by J. Mactear.

"On the Action of Ethyl Chlorocarbonate on some Oxygenated Haloïd Compounds of the Fatty Series:" by O'Neill T. Kelly.

"Laboratory Notes:" by H. E. Armstrong.

Donations to the Library, 1877–78:—

"Handbook of Modern Chemistry, Organic and Inorganic:" by Dr. C. Meymott Tidy: from the Author.

"Animal Chemistry, or the Relations of Chemistry to Physiology and Pathology:" by Charles T. Kingzett, F.I.C., F.C.S., &c.: from the Author.

"The Organic Constituents of Plants, and their Chemical Analysis:" by G. C. Wittstein; translated by Barron F. von Mueller: from the Translator.

"A Key to the Organic Materia Medica:" by Dr. John Muter: from the Author.

"Cooley's Cyclopædia of Practical Receipts." Sixth Edition; revised and partly re-written: by R. V. Tuson. from the Editor.

"Universal Pharmacopœia:" by E. R. Squibb, M.D.: from the Author.

"The London Water Supply:" by Dr. C. Meymott Tidy: from the Author.

"The Water Supply of Tokio, Japan:" by R. W. Atkinson, B.Sc.: from the Author.

"Technical Training:" by Thomas Twining: from the Author.

"Science for the People:" by Thomas Twining: from the Author.

"Science made Easy; a Series of Lectures on the Elements of Scientific Knowledge most required in Daily Life." Parts II and IV: by Thomas Twining: from the Author.

"Description of Plans of the Chemical Laboratories at the Owens College, Manchester: from Professor Roscoe.

"Astronomical Observations made at the Royal University, Edinburgh:" by Piazzi Smyth, F.R.S.E., vol. xiv, 1876–77: from the Royal Observatory.

"Catalogue of the Library of the Museum of Practical Geology and Geological Survey:" compiled by Henry White and Thomas W. Newton: from the Museum of Practical Geology.

"Bristol Museum and Library Catalogue of Books:" from the Council of the Museum.

"Catalogue of the American Philosophical Society's Library:" Part III, Class VI: from the Society.

"The Progress and Resources of New South Wales:" by Charles Robinson, Esq.: from the Author.

"Die geognostische Durchforschung Baeyerns:" von C. W. Gümbel: from the Royal Bavarian Academy of Sciences.

"Meddelelser fra Universitets Kemiske Laboratorium:" ved. P. Waag.

"Om Lavoisier og den Franske Chemi:" af. Th. Hiortdahl: from the Royal Danish Academy of Sciences.

"La Nouvelle Société Indo-chinoise," fondée par le Marquis de Croizier; et son ouvrage "L'Art Khymer:" from the Society.

Pamphlets:—

"On some Tellurium and Vanadium Minerals:" by F. A. Genth: from the Author.

"The Composition of the Buxton Limestones, and of the Limes suitable for the Manufacture of Bleaching Powder:" by R. Lawrence and C. Clarke Hutchinson: from the Authors.

"The Contact Theory of Voltaic Action:" by W. E. Ayrton and John Perry: from the Authors.

"Experimental Researches on the Electric Discharge with the Chloride of Silver Battery:" by Dr. Warren De la Rue and Dr. Hugo Müller: from the Authors.

"Note on Hydrobromic Acid:" by E. R. Squibb, M.D.: from the Author.

"On the Formation and Composition of Complex Oxides of Nickel and Cobalt:" by Thomas Bayley.

"On the Colour Relations and Colorimetric Estimation of Nickel and Cobalt:" by Thomas Bayley.

"On the Colour Relations of Copper and its Salts:" by Thomas Bayley.

"On the Analysis of Alloys containing Copper, Zinc, and Nickel:" by Thomas Bayley.

"On the Volumetric Estimation of Chromium:" by Thomas Bayley: from the Author.

"On Schützenberger's Process for the Volumetric Estimation of Oxygen in Water:" by Christopher Clarke Hutchinson: from the Author.

"Fluid Extracts by Re-percolation:" by E. R. Squibb, M.D.: from the Author.

"Curara, the supposed Remedy for Rabies:" by James Moss, F.C.S.: from the Author.

"The Constitution of Malt-liquors, and their Influence upon Digestion and Nutrition:" by J. J. Coleman: from the Author.

"A Novel View of the Causes producing Typhoid Fever, &c.:" by John Morton, M.B.: from the Author.

"Malaria and Struma in their Relation to the Etiology of Skin Diseases:" by L. P. Yandell, Jun., M.D.: from the Author.

"On Diet and Hygiene in Diseases of the Skin:" by L. Duncan Bulkley, A.M., M.D.

"On the Use of the Solid Rubber Bandage in the Treatment of Eczema and Ulcers of the Leg:" by L. Duncan Bulkley, A.M., M.D.: from the Author.

"The Worth of Life: an Address delivered to the Leeds Literary and Philosophical Society:" by William, Lord Archbishop of York: from the Leeds Literary and Philosophical Society.

"L'Acide Salicylique, et ses Diverses Applications:" par A. Schlumberger: from the Author.

"Sull'Azione della forza detta catalitica, spiegata secondo la Teoria Termodinamica."

"Ricerche fisico-chimiche sui differenti state allotropici dell Idrogeno."

"Reduzione del Cloruro di Argento e del Cloruro ferrico."

"Reduzione dei Clorati in Cloruri."

"Reduzione del Clorale:"

Note del dottore Donato Tommasi: from the Author.

"Estudio sobre la Goma del Quebracho Colorado (*Loxopterigium Lorentii*, Gris.):" par Pedro N. Arata: from the Author.

Periodicals:—

"Philosophical Transactions for 1877:" from the Royal Society.

"List of Officers and Fellows of the Royal Society for 1876:" from the Royal Society.

"Transactions of the Royal Society of Edinburgh." Vol. xxviii, Part I (1876–77).

"Proceedings of the same. Session 1876–1877:" from the Society.

"Quarterly Journal of Science," Vol. viii: from the Editor.

"Quarterly Journal of Microscopical Science, 1878:" from the Microscopical Society.

"The American Journal of Microscopy, January, 1878:" from the Editor.

"Quarterly Journal of the Geological Society, 1877—78:" from the Society.

"Journal of the Iron and Steel Institute, 1878," No. 1: from the Institute.

"Year-book of Pharmacy, 1877:" from Professor Attfield.

"Pharmaceutical Journal and Transactions." Third series, Vol. vii: from the Pharmaceutical Society.

"Journal of the Society of Arts, 1877-78:" from the Society.

"The Textile Colourist." Edited by Charles O'Neile, F.C.S., 1878: from the Editor.

"The Mineralogical Magazine, 1878:" from the Mineralogical Society.

"Nature, 1877–78:" from the Editor.

"The Chemical News, 1877–78:" from the Editor.

"The Telegraphic Journal and Electrical Review, 1877–78:" from the Editor.

"The Telegraphic Pocket-book for 1878:" from the Publishers.

"The Analyst, 1878:" from the Editors.

"Engineering, 1877–1878:" from the Editor.

"The Druggist, 1878:" from the Editor.

"The Chemist and Druggist, 1878:" from the Editor.

"Forty-fifth Report of the Royal Cornwall Polytechnic Society, 1877:" from the Society.

"Newcastle-upon-Tyne Chemical Society: General Meeting, October 24, 1878:" from the Society.

"Annual Report of the Department of Mines, New South Wales, for 1877:" from the Department.

"American Journal of Science and Arts." Vols. xiv, xv: from the Editors.

"Journal of the Franklin Institute, 1878:" from the Institute.

"Proceedings of the American Philosophical Society, December, 1877–78:" from the Society.

"Journal of the Cincinnati Society of Natural History, April, 1878:" from the Society.

"Transactions of the Connecticut Academy of Arts and Sciences, 1878." Vol. iii, Part 2: from the Academy.

"Proceedings of the American Academy of Arts and Sciences," New Series, Vol. v, Parts 2 and 3: from the Academy.

"Mémoires et Comptes rendus de la Société des Sciences Médicales de Lyons." Tome xvi, 1876: from the Society.

"Moniteur Scientifique, 1877–78:" from the Editor.

"Revue Scientifique, 1878:" from the Editor.

"Les Mondes, 1876–77:" from the Editor.

"Bulletin de la Société Industrielle de Mulhouse, December, 1878:" from the Society.

"Bulletin de l'Académie Royale des Sciences de Belgique, 1876–1877:" from the Academy.

"Annuaire de l'Académie Royale des Sciences de Belgique, 1876–1877:" from the Academy.

"Correspondence Scientifique, 1877–78:" from the Editor.

"Archives Néerlandaises des Sciences Exactes et Naturelles." Tome xii: from the Editor.

"Memorie dell' Accademia delle Scienze dell' Istituto di Bologna." Serie 3. Tomi vii, viii, ix: from the Academy.

"Rendiconti delle Sessioni della stessa Accademia, 1876–77 e 1877–78:" from the Academy.

"Boletin de la Institucion libre de Ensenanza, 1878:" from the Editor.

"La Gaceta Cientifica de Venezuela, Febrero, 1878:" from the Editor.

"La Emulacion." Tomo iii. Numero 14: from the Medico-Pharmaceutical Society of Yucatan.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften." 37-ter Band: from the Academy.

"Sitzungsberichte derselben," 1874. Zweite Abtheilung, Nos. 8—10, lxxix Band, 3–5 Heft; lxxx Band, 1–5 Heft.

"Abhandlungen der Königlich-Baeyrischen Akademie der Wissenschaften." 13-ter Band. Erste Abtheilung. 1876:
from the Academy.

"Sitzungsberichte derselben, 1877:" from the Academy.

"Jenaische Zeitschrift für Naturwissenschaft." 12-ter Band. Supplement: from the Editor.

"Verhandlungen der Naturforschenden Gesellschaft in Basel." 6-tes Theil. 6-ter Heft (1878): from the Society.

"Verhandlungen der Physikal-Medicinischen Gesellschaft zu Würzburg." 11-ter Band. 3 und 4 Heft: from the Society.

"Mandblaad voer Naturwetenschappen, 1877–78:"
from the Philosophical Society of Amsterdam.

"Oversigt over det Kongelige Danske Viderskabernes Selskabs Forhandlinger, og des Medlemmers Arbeeten, 1876–1877:"
from the Royal Danish Academy of Sciences.

"Handels Kemisten i Stockholm Berättelse, 1877:"
from Dr. Sedgewick.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS. 1878.

B.

Baker, H., fluorine-compounds of vanadium, 388.
Bayley, T., the behaviour of metallic solutions with filter-paper, and on the detection of cadmium, 304.
Bell. See Watts.
Blyth, A. W., the temperatures at which some of the alkaloïds, &c., sublime, as determined by an improved method, 313.
Bowrey, J. J., poisonous principle of *Urechites suberecta*, 252.
Buchanan, J. Y., laboratory experiences on board the "Challenger," 445.

C.

Carnelley, T., high melting points, 273.
—— tetrabromide of tin, 55.
Carnelley, T., and W. C. Williams, on the determination of high boiling points, 281.
Cross, C. F., and S. Sigiura, action of the halogens at high temperatures upon metallic oxides, 405.
Crow, J. K., derivatives of allylacetone, 53.

D.

Dobbie. See Ramsey.
Dobbin. See Frankland.

E.

Esilman. See Spence.

F.

Fenton, H. J. H., action of hypochlorites on urea, 300.
Fisher, W. W., manganese tetrachloride, 409.
Foster, W., action of alkaline hypobromite on ammonium salts, urea, and oxamide. Part I, 470.
Frankland, E., and L. Dobbin, constitution of the olefine produced by the action of zinc upon ethylic iodide, 545.
Frankland, E., and L. Thorne, luminosity of benzol when burnt with non-luminous combustible gases, 89.

G.

Gladstone, J. H., and A. Tribe, action of the copper-zinc couple on alkaline oxy-salts, 139.
—— —— analogies between the action of the copper-zinc couple and of occluded and nascent hydrogen, 306.
Groves. See Stenhouse.

H.

Hannay, J. B., action of bromine upon sulphur, 284.
—— a new manganese reaction, 269.
—— a new process for the volumetric estimation of cyanides, 245.
Harrow, G. H. U., on pyrotritartaric and carbopyrotritartaric acids, products of the action of dilute sulphuric acid on diacetosuccinic ether, 425.
Hodgkinson, W. R., action of sodium on the benzyl ether of isobutyric acid, 495.

J.

Johnson, G. S., ammonium triiodide, 397.
—— polyiodides, 183.
Jones, F., action of reducing agents on potassium permanganate, 95.

Jones, H. C., a simplification of Regnault's method for determining boiling points with small quantities of substance, 175.

K.

Kingzett, C. T., the chemistry of cocoa-butter. Part I. Two new fatty acids, 38.
Kingzett. See also Paul.

L.

Luff. See Wright.

M.

Mactear, J., on the part played by carbon in reducing the sulphates of the alkalis, 475.
Menke, A. E., preparation of salts of nitrous oxide, 401.
Mills, E. J., potable waters, 57.
Mills, E. J., and D. Wilson, action of oxides on salts. Part I, 360.
Muir, M. M. P., a fourth method for estimating bismuth volumetrically, 70.
—— bismuth compounds, 192.
—— influence exerted by time and mass in certain reactions in which insoluble salts are produced, 27.
Muir. See also Sigiura.

P.

Patterson. See Wright.
Paul, B. H., and C. T. Kingzett, tannins, 217.
Perkin, W. H., action of ammonia on anthrapurpurin, 216.
—— derivatives of anisoïl (anisol), 211.
Pickering, S., action of sulphuric acid on copper, 112.

R.

Ramsay, W., and J. J. Dobbie, decomposition-products of quinine, 102.
Riley, E., estimation of phosphorus in iron and steel, 104.
Roemer. See Schunck.

S.

Schunck, E., and H. Roemer, madder colouring matters (continuation), 422.
Senier, A., and A. J. G. Lowe, a new test for glycerin, 438.
Sigiura, S., and M. M. P. Muir, on essential oil of sage, 292.
Sigiura. See also Cross.
Sorby, H. C., on the determination of the index of refraction of liquids by means of the microscope, 487.
Spence, P., and A. Esilman, on the detection and estimation of free mineral acids in various commercial products, 298.
Stenhouse, J., and C. E. Groves, contributions to the history of the naphthalene series. No. II. β-Naphthaquinone, 415.

T.

Thomas, J. W., action of hydrochloric acid upon various metallic salts, 367.
—— on cuprous chloride and the absorption of carbonic oxide and hydrochloric acid gas, 72.
Thorne. See Frankland.
Tilden, W. A., on the hydrocarbons obtained from the *Pinus sylvestris*, with remarks on the constitution of the terpenes, 80.
—— terpin and terpinol, 247.
Tribe. See Gladstone.

V.

Vines, S. H., on the chemical aspect of vegetable physiology, 375.

W.

Warington, R., nitrification, 44.
Watts, C. W., and C. A. Bell, preparation of metallic chlorides, 442.
Williams. See Carnelley.
Wilson. See Mills.
Witt, O. N., aromatic nitrosamines, 202.
Wright, C. R. A., and A. P. Luff, alkaloïds of the aconites. Part II. Alkaloïds contained in *Aconitum ferox*, 151.
—— —— the alkaloïds of the aconites. Part III, 318.
—— —— the alkaloïds of the veratrums.

Part I. The alkaloïds of *Veratrum sabadilla* (*Asagræa officinalis*), 338.

Wright, C. R. A., and A. P. Luff, first report to the Chemical Society on "Researches on some points in chemical dynamics," 1.

—— —— second report to the Chemical Society on "Researches on some points in chemical dynamics," 504.

Wright, C. R. A., and Geo. Patterson, citric acid as a constituent of the juice of unripe mulberries, 78.

Y.

Young, T. Graham, the gas of the "Grotta del Cane," near Naples, 51.

INDEX OF SUBJECTS.

TRANSACTIONS. 1878.

A.

Absorption of carbonic oxide and hydrochloric acid by cuprous chloride, 72.
Acetyl-apoaconitine, 327.
Acetyl-apopseudaconitine, 168, 170.
—— salts of, 169.
Acids, free mineral, detection and estimation of, in various commercial products, 298.
—— vegetable, in the cells of plants, 383.
Acolyctine, 335.
—— Hübschmann's, 337.
Aconelline, 335.
Aconine, 318.
—— action of acids on, 326.
—— action of organic acid anhydrides on, 337.
—— analysis of, 321.
—— properties of, 320.
—— salts, 322.
—— action of benzoic and acetic anhydrides on, 326.
—— and pseudaconine, qualitative reactions of, 323.
Aconite roots, alkaloïd constituents of, 333, 336.
Aconitine, action of acids on, 324.
—— action of organic acid anhydrides on, 337.
—— action of saponifying agents on, 152, 318, 336.
—— other bases contained in commercial, 174.
—— action of benzoic and acetic anhydrides on, 326.
Alkalis, sulphates of, the part played by carbon in reducing, 475.
Alkaloïd constituents of aconite roots generally, 333, 336.
Alkaloïds contained in *Aconitum ferox*, 151.
—— &c., temperatures at which some sublime, as determined by an improved method, 313.
—— of the aconites, 151, 318.
—— from sabadilla seeds, isolation of, 341.
Alkaloïds of the veratrums, *Veratrum sabadilla* (*Asagræa officinalis*), 338.
Allyl acetone, preparation of, 53.
—— —— secondary alcohol from, 54.
Allyl alcohol, homologue of, 54.
Amidoalizarin, or anthrapurpuramide, 217.
Ammonium fluoxyhypovanadate, 395.
—— fluoxyvanadate, 391.
—— —— acicular, 393.
—— —— lamellar and pyramidal, 392.
Ammonium nitrate, action of copper-zinc couple on, 150.
—— triiodide, 397.
—— —— properties of, 399.
Anisoïl (anisol), new derivatives of, 211.
Anniversary meeting, March 30th, 1878, 221.
Anthrapurpuramide or amidoalizarin, 217.
Anthrapurpurin, action of ammonia on, 216.
Apoaconitine, 318, 324, 336.
Apopseudaconine, 165.
Apopseudaconitine, 152, 167, 336.
Asparagine in plants, 386.
Atisine, 335.

B.

Balance-sheet of the Chemical Society (1877–1878), 243.
—— —— of the Research Fund (1877–1878), 244.
Barium periodate, basic, 409.
Benzene, luminosity of, when burnt with non-luminous combustible gases, 89.
Benzoic acid, 499, 502.
—— —— from a mixture of pseudaconitine and apopseudaconitine, 162.
Benzoyl-apoaconitine, 327.
Benzoyl-apopseudaconitine, 171.
Benzoyl-cevadine, 351.
Benzyl benzyl-dimethacetate, action of sodium on, 499.
—— —— saponification of, 500.
Benzyldimethyl-benzyl acetate, 498.

Benzyl isobutyrate, action of sodium on, 497.
—— —— preparation of, 496.
Bismuth, estimation of, volumetrically, 70.
—— oxalate, action of hot water on, 70.
—— —— basic, 195.
—— —— normal, 70, 194.
—— trichloride, action of chromyl dichloride on, 193.
—— —— action of sulphur chloride on, 193.
—— —— action of sulphur dioxide on, 193.
Bismuthic hydrate, red, 199.
Bismuthous iodide, 200.
—— oxyiodide, red, 201.
Bismuthyl chloride, 193.
—— —— action of hydriodic acid on, 201.
—— dioxalate, 197.
—— iodide, 201.
Boiling-points, simplification of Regnault's method for determining, 175.
Bromine on sulphur, action of, 284.

C.

Cadmium, detection of, 304.
Calcium periodate, basic, 409.
Calculation of heat disturbances during the reduction of oxides, 3.
Camphor, relation of, to terpenes, 88.
Carbohydrates in plants, decomposition of, into acids and oxybenzenes, 386.
Carbon, the part played by, in reducing the sulphates of the alkalis, 475.
Carbon-hydrogen, action on potassium chlorate, 310.
—— —— action of, on potassium ferricyanide, 311.
Carbonic oxide, absorption of, by cuprous chloride, 72.
—— —— benzolised, 91.
—— —— temperature of the flame of, 94.
Carbopyrotritartaric acid, 425, 431.
—— —— behaviour of, when heated, 433.
—— —— fused with potassium hydroxide, 435.
Cevadic acid, 339, 342, 347.
—— —— action of fused potash on, 349.
Cevadilline, 343.
—— composition and derivatives of, 355.
Cevadine, 342, 344.
—— (the "veratrine" of Merck, and of Schmidt and Köppen), composition and derivatives of, 344.
Cevadine, aurochloride, 346.
—— preparation of, 342.
Cevillin, 357.
Cevine, 347.
Chemical dynamics, second report on some points in, 504.
—— —— researches on some points in, 1.
Chlorophyll, 375.
—— conversion of, into a carbohydrate, 381.
—— corpuscles, coloration of, 381.
—— —— starch-grains in, 376.
—— presence and mode of origin in parasitic and saprophytic plants, 381.
Chromic chloride, preparation of, 444.
Citrates in solution, action of hydrochloric acid on, 374.
Citric acid, a constituent of the juice of unripe mulberries, 78.
Cobalt monoxide, action of carbon oxide, carbon, and hydrogen on, 535.
—— oxides, preparation of, 533.
—— sesquioxide, action of carbon oxide, carbon, and hydrogen on, 536.
Cocoa butter, chemistry of, 38.
—— —— new fatty acids from, 38.
Colouring matter from pseudaconine, 160.
Copper, action of sulphuric acid on, 112.
—— agglomeration and deglomeration of, 148.
—— formation of sulphur in the action of sulphuric acid on, 125.
—— influence of an electric current in the action of sulphuric acid on, 126.
—— subsulphide, formation of, in the action of sulphuric acid on copper, 120.
—— sulphide, 115.
Copper sulphides, oxidisability of, 115.
Copper-zinc couple, action of, on alkaline oxy-salts, 139.
—— —— action of, on nitrobenzene, 306.
—— —— action of, on potassium chlorate, 147.
—— —— analogies between its action and that of occluded and nascent hydrogen, 306.
—— —— use of, in the detection of chlorates, 147 (note).
—— —— use of, in testing for nitrates, 142.
Cupric oxide, preparation of, 6.
Cuprous chloride, absorption of carbonic oxide and hydrochloric acid gas by, 72.
—— oxide, preparation of, 7.

Cutch from *Acacia catechu*, action of sulphuric acid on, 219.
—— glucose in, 219.
Cyanides, new process for the volumetric estimation of, 245.

D.

Dextrin in the cells of plants, 383.
Diacetosuccinic ether, action of dilute sulphuric acid on, 425.
Diacetyl-apopseudaconine, 330.
Dibenzoyl-apopseudaconine, 330.
Dibromopurpuroxanthin, 424.
Dicarbopyridenic acid, 102.
Dimethylprotocatechuic acid from pseudaconitine, 152, 160, 166.
—— —— from veratrine, 353.
Dimethylpyrocatechin from dimethylprotocatechuic acid, 162.
Dinaphthyldiquinhydrone, 417, 420.
Dinaphthyldiquinol, 419.
Dinaphthyldiquinone, 419.
Dinitrodiphenylamine, 208.
Diphenylhydrazine, 203.
Diphenylnitrosamine, 202.
—— action of aniline or other primary monamine on, 203.
Diquinols, 422.
Donations to the library of the Chemical Society (1877–1878), 552.
Drainage from land unmanured and uncropped, 67.

E.

Earth-metals, alkaline, action of iodine on their oxides and carbonates, 409.
Electrolysis of nitrate of potassium, 145.
Estimation of carbonic anhydride in sea-water, 460.
Ethyl acetosodacetate, preparation of solid, 426.
—— carbotritartrate, 433.
—— diacetosuccinate, action of dilute sulphuric acid on, 426, 428.
—— —— preparation of, 427.
—— pyrotritartrate, 431.
Ethylene, constitution of, 545.
Etiolin, 381.
Evaporator for water analysis, 62.

F.

Fatty acids from cocoa butter, 38.
Ferric oxide, preparation of, 8.
Ferroso-ferric oxide, action of carbon-oxide, carbon, and hydrogen on, 508.
—— —— preparation of, 508.
Ferrous oxide, action of carbon oxide, carbon, and hydrogen on, 506.
—— —— action of a mixture of carbon monoxide and dioxide on, 505.
—— —— preparation of, 505.
Filter paper, the behaviour of metallic solutions with, 304.
Fluoxyvanadates, 389—395.

G.

Gas of the Grotta del Cane, 51.
Glass, compressibility of, 456.
Glycerin, a new test for, 438.
Grotta del Cane, gas of, 51.

H.

Halogens, action of, at high temperatures on metallic oxides, 405.
Hexnitrodiphenylamine, 209.
High boiling points, determination of, 281.
—— melting points, 273.
Hydrocarbons from the *Pinus sylvestris*, 80.
Hydrochloric acid gas, absorption of, by cuprous chloride, 72.
Hydrogen, analogies between the action of the copper-zinc couple and of occluded and nascent, 306.
—— benzolized, 90.
—— condensation of, by finely-divided copper, 148.
—— temperature of the flame of, 94.
Hypobromite, alkaline, action of, on ammonium salts, urea, and oxamide, 470–474.

I.

Index of refraction of liquids, determination of, by means of the microscope, 487.
Iron, magnetic oxide of, preparation of, 508.
Isoanthraflavic acid, 217.
Isobutyric acid, 498, 501.

J.

Jervine, 335.

L.

Laboratory experiences on board the "Challenger," 445.
Lead acetate, action of, on iodine in potassic iodide, 189.
—— dioxide, action of carbon oxide, carbon, and hydrogen on, 531.
—— monoxide, action of carbon oxide, carbon, and hydrogen on, 527.
—— oxides, action of bromine and air on, 406.
—— —— action of chlorine and air on, 407.
—— —— action of halogens on, 405.
—— —— action of a mixture of iodine vapour and air on, 405.
—— —— preparation of, 527.
—— oxyiodide, 397.
Leucophyll, 379.
Liquids, determination of the index of refraction of, by means of the microscope, 487.
Lycoctonine, 335.

M.

Madder colouring matters, 422.
Malic acid in the juice of unripe mulberries, 78.
Manganate of iron and manganese (double), 269.
Manganese dioxide, action of carbon oxide, carbon, and hydrogen on, 515.
—— —— crystallised, artificial production of, 271.
—— —— preparation of, 513.
—— oxide, composition of, formed by ignition in air of higher and lower manganese oxides, 525.
—— oxides, 512.
—— reaction, a new, 269.
—— red oxide of, action of hydrochloric acid on, 413.
—— sesquioxide, action of hydrochloric acid on, 413.
—— tetrachloride, 409.
Manganoso-manganic oxide, 270.
—— —— oxides, action of carbon oxide, carbon, and hydrogen, on, 520.
—— —— —— preparation of, 520.
Manganous manganate, 269.
—— oxide, action of carbon oxide, carbon, and hydrogen on, 523.
—— —— preparation of, 523.
Marsh gas, benzolized, 91.
—— —— from sodium acetate, analysis of, 91.
Mass, influence of, in the production of insoluble salts, 27.
Mercury, sea-water, sodium chloride solution and distilled water, relative apparent compressibility of, 452.
Metallic chlorides, preparation of, 442.
—— oxides, absorption of CO and CO_2 by, 540.
—— —— action of halogens on, at high temperatures, 405.
—— salts, action of hydrochloric acid on, 367.
—— solutions, behaviour of, with filter-paper, 304.
Methylcrotonic acid, 339, 349.
α-methylorthoxyphenylacrylic acid, action of hydriodic acid on, 215.
Methylorthoxyphenylcrotonic acid, action of hydrobromic acid on, 212.
Mimosa bark, action of sulphuric acid on, 219.
—— —— an organic acid from, by the acid of sulphuric acid on, 219.
Mimotannic acid, 219.
Mononitrodiphenylamine, 205.
Mononitrodiphenylnitrosamine, 206.
—— action of bromine on, 206.
Munjistin, action of reagents on, 424.
—— and purpuroxanthic acid, identity of, 422.

N.

Nickel monoxide, action of carbon oxide, carbon, and hydrogen on, 538.
—— oxides, preparation of, 537.
—— sesquioxide, action of carbon oxide, carbon, and hydrogen on, 539.
Napelline (Hübschmann's), 335, 337.
Naphthalene series, contributions to the history of, 415.
β-Naphthaquinone, 415.
Nitrification, 44.
—— influence of light on, 49, 50, 51.
—— of an ammonium salt, 50.
—— prevention of, by carbon bisulphide, 48, 49.
—— prevention of, by chloroform vapour, 46, 49.
Nitrobenzene, detection of small quantities of, 307 (*note*).
Nitro-*β*-naphthaquinone, 416.
Nitrosamines, aromatic, 202.
Nitrous oxide, preparation of salts of, 401.

O.

Obituary notices of deceased fellows, 227.
Oil of sage, essential, 292.
Olefine, constitution of, produced by the action of zinc on ethyl iodide, 545.
Oleum foliorum Pini sylvestris, 82.

Orthallylanisoïl, 212.
Orthobutenylanisoïl, 213.
Orthovinylanisoïl, 211.
Oxalates in solution, action of hydrochloric acid on, 374.
Oxalic acid, action of, on the permanganates, 98.
Oxidation of quinine with potassium permanganate, 102.

P.

Palladium-hydrogen, action of, on nitrobenzene, indigo, and sulphurous and arsenious acids, 308.
—— —— action on potassium chlorate, 308.
—— —— action on potassium nitrate, 307.
Paravinylanisoïl, 214.
Phosphates, action of hydrochloric acid on, 374.
Phosphorus in iron and steel, estimation of, 104.
Picraconine, 332.
Picraconitine, action of saponifying agents on, 336.
—— decomposition-products of, 332.
Piezometer, 448.
Plants, decomposition of carbohydrates in, 386.
—— formation of acids in, 385.
—— formation of formic aldehyde in the cells of, 380.
—— parasitic and saprophytic, presence and mode of origin of chlorophyll in, 381.
—— presence of pyrocatechin in, 380.
Platinum-hydrogen, action on potassium chlorate, 308.
—— action on potassium ferricyanide, nitrobenzene, and arsenious and sulphurous acids, 310.
—— action on potassium nitrate, 309.
Plumboso-plumbic oxide, action of carbon oxide, carbon, and hydrogen on, 530.
Polyiodides, 183.
Potable waters, 57.
—— —— effect of filtration through spongy iron, 66.
—— —— influence of size of evaporating basin, 60.
—— —— natural constants of, 64.
—— —— probable error in analysis of, 58.
Potassium bismuthates, 197.
—— chlorate, action of copper-zinc couple on, 147.
—— —— electrolysis of, 147.
Potassium cyanate, action of calcium hypochlorite or hypobromite on, 302.
—— fluoxyvanadate, acicular, 390.
—— fluoxyvanadate, lamellar, 389.
—— iodide and iodine, action of lead acetate on, 189.
—— nitrate, action of the copper-zinc couple on, 139.
—— permanganate, action of ammonia on, 96.
—— —— action of arsenic on, 97.
—— —— action of ferrous salts on, 100.
—— —— action of hydrogen on, 95, 96.
—— —— action of manganese chloride on, 100.
—— —— action of oxalic acid on, 99.
—— —— action of phosphine on, 97.
—— —— action of reducing agents on, 95.
—— —— action of stibine on, 98.
—— silver polyiodide, 184, 186.
—— thallium polyiodide, 187.
—— triiodide, 184.
—— —— action of ammonia on, 397.
Pseudaconine, 160.
—— action of alcoholic soda on, 160.
—— action of benzoic and acetic anhydrides on, 330.
—— action of organic anhydrides on, 170, 337.
—— and aconine, qualitative reactions of, 323.
Pseudaconitine, action of acids on, 166.
—— action of alkalis on, 160.
—— action of glacial acetic acid on, 169.
—— action of inorganic acids on, 168.
—— action of organic anhydrides on, 170, 337.
—— action of saponifying agents on, 165, 336.
—— and its derivatives, constitution of, 172.
—— composition of, 151.
—— dimethylprotocatechuic acid from, 160, 166.
—— preparation of, 152, 154.
Purpurinamide, 424.
Purpuroxanthic acid and munjistin, identity of, 422.
Pyrolusite, 269.
—— action of carbon oxide, carbon, and hydrogen on, 518.
Pyrotritartaric or uvic acid, 425, 428.

Q.

Quinetin, Marchand's, 104.
Quinine, action of potassium permanganate on, 102.

R.

Rain-water off the north coast of New Guinea, atmospheric contents of, 467.
Regnault's method for determining boiling points, simplification of, 175.
Research Fund Committee, report of, 239.

S.

Sabadilla seeds, constitution of the uncrystallisable base from, 357.
Sabadilline, 339.
Sabatrine, 339.
Sage, essential oil of, 292.
Salts, action of hydrochloric acid on, 367.
— inorganic, melting points of, 275.
— insoluble, influence of time and mass in producing, 27.
Salviol, 295.
— action of hydrochloric acid, bromine, and phosphorus pentoxide on, 296.
— action of nitric acid on, 295.
Sea-depths, sounding of, 448.
Sea-water, atmospheric contents of, 456.
— compressibility of, 451.
— sodium chloride, solution of mercury and distilled water, relative apparent compressibility of, 452.
— tables of the atmospheric contents of, 462, 464.
Silicic oxide, action of, on potassium carbonate, 362.
Silver carbotritartrate, 432.
— hyponitrite, 401.
— potassium polyiodide, 184, 186.
— pyrotritartrate, 429.
Sodium carbotritartrate, 432.
— chloride, solution of sea-water, mercury, and distilled water, relative apparent compressibility of, 452.
— hyponitrite, 402.
— — reactions of, with some of the metals, 404.
— pyrotritartrate, 430.
Stannic bromide, preparation of, 444.
— chloride, preparation of, 442.
Starch-grains in chlorophyll-corpuscles, 376.
Sugar in the cells of plants, 383.
Sulphates in solution, action of hydrochloric acid on, 372.
Sulphur, action of bromine on, 284.
— action of bromine on, in presence of arsenic, 291.
Sulphuric acid, action of, on copper, 112.
Sylvestrene from Swedish turpentine oil, 82.

T.

Tannin, estimation of, 217.
Tannins, notes on, 217.
Tartrates in solution, action of hydrochloric acid on, 374.
Temperature of initial action of carbon on copper and iron oxides, determination of, 16.
Temperature of initial action of carbon oxide on copper and iron oxides, determination of, 8.
Temperature of initial action of hydrogen on copper and iron oxides, determination of, 12.
Terpenes, constitution of, 83.
— from essential oil of sage, 293, 297.
— relation of, to camphor, 88.
Terpin, 247.
— action of dilute hydrochloric acid on, 248.
— action of sulphuric acid on, 250.
— hydrate, oxidation of, 87.
Terpinol, 247, 248.
— dichloride, 249.
Terpinylene, 251.
Tetranitrodiphenylamine, 209.
Theobromic acid, 44.
Time, influence of, in the production of insoluble salts, 27.
Tin, tetrabromide, preparation and properties of, 55.
Titanic chloride, preparation of, 443.
— oxide, action of, on potassium carbonate, 365.
Toluene, 497.
Tungstic oxide, action of, on potassium carbonate, 361.
Turpentine oil, Russian, 80.

U.

Urea, action of hypochlorites on, 300.
Urechites suberecta, poisonous principle of, 252.
Urechitin, 265.
Urechitin, preparation of, 255.
Urechitoxetin, 262, 264.
Urechitoxin, preparation of, 252.
— amorphous, 252, 265.
— colour reaction of, 263.
— properties of, 258.
— pseudo-amorphous, 261.
Uvic or pyrotritartaric acid, 428.

V.

Vanadium, some fluorine-compounds of, 388.

University of Michigan

Vegetable physiology, chemical aspect of, 375.
Veratria, action of alcoholic soda on, 338.
Veratric acid, 339, 342, 353.
Veratrine, 339.
—— (of Couerbe), 343.
—— or cevadine, 342.
—— composition and derivatives of, 352.
—— salts of, 353.
Veratrum Sabadilla, alkaloïds of, 338.
Veratrums, alkaloïds of the *Veratrum Sabadilla* (*Asagræa officinalis*), 338.
Verine, 354.

W.

Water, distilled, sea-water, sodium chloride solution and mercury, relative apparent compressibility of, 452.
Waters from deep wells, organic analyses of, 64.
—— potable, 57.
—— —— effect of filtration through spongy iron, 66.
—— —— influence of size of evaporating basin, 60.
—— —— natural constants, 64.
—— —— probable error in analysis, 58.
Wells, deep, in the chalk, organic analyses of waters from, 64.
—— —— in the Devonian, millstone grit, and coal measures, organic analyses of waters from, 66.
—— —— in the new red sandstone, organic analyses of waters from, 67.

Z.

Zinc fluoxyvanadate, 394.

ERRATUM.

Page	Line	
226 549	16 27	*for* "On a New Method for the Determination of Boiling Points:" by W. Jones, *read* "On a Simplification of Regnault's Method for Determining Boiling Points with Small Quantities of Substance:" by H. Chapman Jones.

HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY, ST. MARTIN'S LANE.